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Request for grant of a patent

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1.	Your reference	~~9829 GB~~ / SMS
2.	Patent application number *(The Patent Office will fill in this part)*	0326286.2 11 NOV 2003
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	Vantico GmbH Klybeckstrasse 200 4057 Basle Switzerland
	Patents ADP number *(if you know it)*	~~80169000~~ 08746257001
	If the applicant is a corporate body, give the country/state of its incorporation	Switzerland
4.	Title of the invention	Initiator systems for polymerisable compositions
5.	Name of your agent *(if you have one)* "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Abel & Imray 20 Red Lion Street London WC1R 4PQ
	Patents ADP number *(if you know it)*	174001

		Country	Priority application number *(if you know it)*	Date of filing *(day/month/year)*
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number			

		Number of earlier application	Date of filing *(day/month/year)*
7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application		

8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as an applicant, or* *c) any named applicant is a corporate body.*	YES

9.	Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.	
	Continuation sheets of this form	0
	Description	33
	Claim*(s)*	8
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10.	If you are also filing any of the following, state how many against each item.	
	Priority documents	
	Translations of priority documents	
	Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
	Request for preliminary examination and search *(Patents Form 9/77)*	1
	Request for substantive examination *(Patents Form 10/77)*	
	Any other documents *(please specify)*	
11.		I/We request the grant of a patent on the basis of this application. Signature: Abel & Imray Abel & Imray Date: 11 November 2003
12.	Name and daytime telephone number of person to contact in the United Kingdom	Susan M Scott 020 7242 9984

Initiator systems for polymerisable compositions

The present invention relates to complexes of organoboranes with amino functional organosilicon compounds which are effective polymerisation initiators for radically polymerisable systems, especially acrylate or methacrylate adhesives. The complexes are particularly useful in the preparation of adhesives for bonding low surface energy plastics based on, for example, polyolefins and polyfluoroolefins.

Low surface energy polyolefins such as polyethylene, polypropylene and polytetrafluoroethylene have a variety of attractive properties in a variety of uses. However, because of the low surface energy of these plastic materials, it is very difficult (a detailed description of the difficulties in adhesively bonding these materials can be found in *"Adhesion Problems at Polymer Surfaces"* by D. M. Brewis, appeared in *"Progress in Rubber and Plastic Technology"*, vol. 1, p.1, 1985) to find adhesive compositions, which bond to them. The commercially available adhesives, which are used for these plastics generally, require complex and costly substrate surface pretreatment of the surface before the adhesive will bond to the surface. Such pretreatments include corona discharge, flame treatment, plasma treatment, oxidation by ozone or oxidizing agents, sputter etching and the like. Another approach for adhesively bonding low surface energy substrates is via coating the low surface energy substrate with a material of high surface energy. But, also in this case the low surface energy substrates need to be previously pretreated with one of the aforementioned surface preparation techniques in order to assure adequate adhesion of the primer. All of these techniques can be found in *"Treatise on Adhesion and Adhesives"* by J. D. Minford, Marcel Dekker, 1991, New York, vol. 7, p.333-345). There is therefore a need for adhesive compositions, which are capable of bonding to low surface energy substrates, and bonding low surface energy substrates to other substrates, without the need for extensive or costly surface preparation techniques.

Vinyl polymerization initiated by organoboron compounds has found numerous applications and amongst many, in certain cases it was also used in bonding surfaces of low surface energies. G. Kolesnikov and L. Fedorova [*Bull. Acad. Sci. USSR, Div. Chem. Sci. p. 236 (1957)*] report on the polymerization of acrylonitrile in the presence of tributylborine.

G. Kolesnikov and N. V. Klimentova [*Bull. Acad. Sci. USSR, Div. Chem. Sci. p. 653 (1957)*] investigate the use of trialkylborine as a catalyst for the polymerization of unsaturated compounds.

J. Furukawa et. al. [*J. Polym. Sci. vol. XXVI, No 113, p. 234-236 (1957)*] report on the use of triethylboron as an initiator for vinyl polymerization.

G. Kolesnikov and L. Fedorova [*Bull. Acad. Sci. USSR, Div. Chem. Sci., p. 906 (1958)*], disclose information on the mechanism of the polymerization of acrylonitrile in the presence of tributylborane.

J. Fordham and C. Sturm [*J. Polym. Sci., vol. XXXIII, No 126, p. 503-504 (1958)*] describe the mechanism of trialkylboron-inititated polymerization.

J. Furukawa et. al. [*Macromoleculare Chemie, vol. 31, p. 122 (1959)*] report on the reactivity use of organometallic compounds for olefin polymerization.

I. M. Panayotov [*Comptes Rendus de l' Academie Bulgare des Sciences, vol. 14, No 2, p. 147-150 (1961)*], reports on the cocatalytic activity of some metal salts on vinyl polymerization with triethylboron.

F. Arimoto [*J. Polym. Sci.: Part A-1, vol. 4, p. 275-282 (1966)*], proposes a mechanism for the organoboron compounds initiated polymerization of olefinic monomers.

R. Kern and J. Schafer [*Polym. Lett., vol. 5, p. 157-162 (1967)*], report on the existence of a free radical organoboron complex in the polymerization of methyl methacrylate.

J. Grotewold, E. Lissi and A. Villa [*J. Polym. Sci.: Part A-1, vol. 6, p. 3157-3162 (1968)*], investigates the polymerization mechanism of vinyl monomers in the presence of trialkylboranes.

P. Brindley and R. Pearson [*Polym. Lett., vol. 6, p. 831-835 (1968)*], report on the free-radical polymerization of methyl methacrylate in the presence of trialkylboranes.

T. Dawson, R. Lundberg and F. Welch [*J. Polym. Sci.: Part A-1, vol. 7, p. 173-181 (1969)*], studied the free-radical copolymerisation of 1,2-dichloroethylenes and provide evidence for chain transfer by chlorine atom elimination.

E. Aranchibia et. al. [*J. Polym. Sci.: Part A-1, vol. 7, p. 3430-3433 (1969)*], report on the mechanism of vinyl monomer polymerization in the presence of trialkylboranes and inhibitors.

K. Kojima et. al. [*Polym. Lett., vol. 8, p. 541-547 (1970)* and J. Japan. Chem. Soc., No. 11, p. 2165-2171 (1972)], investigated the polymerization of methyl methacrylate initiated by a trialkylborane-pyridine systems.

E. Abuin et. al. [*Polym. Lett., vol. 7, p. 515-518 (1970)*], report on the polymerization of olefinic monomers initiated by triethylborane-peroxide mixtures.

M. Yoshikuni et. al. [*J. Polym. Sci., vol. 11, p. 3115-3124 (1973)*], investigate the polymerization of methyl methacrylate initiated by tri-n-butylborane-organic halide systems.

S. Iwabuchi et. al. [*Polym. J., vol. 6, No 2, p. 185-190 (1974)*], report on the copolymerisation of vinylhydroquinone and acrylonitrile by tri-n-butylborane.

E. Abuin et. al. [*Eur. Polym. J., vol. 11, p. 779-782 (1975)*], investigate the free radical polymerization in the presence of triethylborane.

T. Sato et. al. [*J. Japan. Chem. Soc., No 6, p. 1080-1084 (1975)*], provide an analysis of the mechanism of radical formation resulted from the initiator system of triethylborane and oxygen by spin trapping technique.

N. Nakabayashi and E. Masuhara [*J. Biomed. Mater. Res., vol. 12, p. 149-165 (1978)*], report on the development of an adhesive pit and fissure sealant based on the polymerization of methyl methacrylate initiated by a tri-n-butyl borane derivative.

S. Ivanchev et. al. [*Polym. Sci. USSR, vol. 22, No 12, p. 8000-8006, (1980)*], study the polymerization of vinyl acetate initiated by alkylborane-oxidizer type systems.

N. Nakabayashi and E. Masuhara [*Biomed. Polym., p. 85-111 (1980)*], report on the preparation of a hard tissue compatible materials (dental polymers).

S. Ivanchev and L. Shumnyi [*Doklady Akademii Nauk. USSR, vol. 270, No 5, p. 1127-1129 (1983)*], report on the mechanism of initiation of polymerization of vinyl monomers by means of the trialkylborane-acid system.

T. Sato et. al. [*Macromol. Chem., 184, p.431-442 (1983)*], report on the application of spin trapping technique to radical polymerization.

Y. Imai et. al. [*J. Dent. Res., vol. 70, No 7, p. 1088-1091 (1991)*], investigate the use of polymerization initiator systems and interfacial initiation of polymerization in adhesive bonding of resin to dentin.

M. Suzuki et. al. [*J. Dent. Res., vol. 70, No 7, p. 1092-97 (1991)*], carried out vibrational analysis studies by Raman spectroscopy studying the interface between dental adhesive resin and dentin.

M. Ozaki et. al. [*Dental Mater. J., vol. 10, No 2, p. 105-120 (1991)*] report on laser-Raman spectroscopic studies of the adhesive interface between 4-MET/MMA-TBB resin and hydroxyapatite or bovine enamel.

D. Rhubright and T. C. Chung [*Proc. Amer. Chem. Soc. Polym. Mater. Sci. Eng., vol. 67, p. 112-113 91992]]* report on the synthesis of functionalized polypropylene and polypropylene-polymethacrylate graft copolymer.

V. Dodonov and D. Grishin [*High Molecular Compounds, vol. 35, No 3, p. 137-141 (1993)*], investigate the polymerization of some vinyl monomers on triisobutylboron-containing radical initiators in the presence of hydroquinone and benzoquinone.

D. Rhubright and T. C. Chung [*Amer. Chem. Soc., Div, Polym. Chem., Proceedings of Chicago (IL) Meeting, vol. 34, No. 2, p. 560-561 (1993)*] study the synthesis of PP-g-PMMA, PP-g-PVA and PP-PCL copolymers.

T. C. Chung [*Polym. Preprints, vol. 35, No 1, p. 674-675 (1994)*], report on the synthesis of functionalized and grafted polyolefin copolymers prepared by transition metal catalysts and borane monomers.

T. Miyokawa et. al. [*Mater. Res. Soc. Symp. Proc., vol. 334, p. 365-371, (1994)*], investigate the photochemical modification of fluorocarbon resin surface to adhere with epoxy resin.

S. Fujisawa [*Chemical Abstract No 88532r, Chemical Abstracts, vol. 73, (1970)*], reports on dental self-curing adhesive compositions comprising methyl methacrylate, organoborane/amine complexes and a compound reactive with the amine (e.g. isocyanate, acid chloride, sulfonyl chloride, etc.).

Y. Imai et al. [*Chemical Abstract No 134385q, Chemical Abstracts, vol. 80, (1974)*], reports on a mixture of methyl methacrylate, tributylboron and optionally poly(methyl methacrylate) and/or water that is used to adhere polyolefin or vinyl polymer articles. Polypropylene, poly(vinyl chloride), polyethylene and poly(vinyl acetate) were bonded.

US 3,007,970 discloses the preparation of metal organoboron compounds, particularly sodium organoboron compounds having at least one ethyl or methyl group.

US 3,275,611 relates to a process for polymerising olefinic compounds using a multiple component catalyst comprising of complexes of amines with organoboron compounds and peroxides or hydroperoxides.

US 3,567,453 describes a radiation sensitive compound which comprises a tetrasubstituted borate anion and an organic cation containing an atom selected from the group consisting of nitrogen, arsenic, tin antimony, sulphur, iodine, phosphorous, oxygen, titanium, palladium, chromium and cobalt. These compounds can be spectrally sensitised and can be used in photoresists and for lithography.

US 4,043,982 discloses polymerizable compositions, which serve as adhesives, sealants, potting compounds, etc., the primary components of which are an acyl peroxide initiator, an arylamine polymerization accelerator, and a polymerizable acrylate-isocyanate monomer.

US 4,307,182 relates to a radiation sensitive element comprising a substrate having coated on at least one side thereof a layer comprising a radiation sensitive tetra(aliphatic) borate salt.

US 4,343,891 describes a method for forming an image that includes the step of desensitising a radiation sensitive imaging system comprising a dye and a tetra(hydrocarbyl)borate in a binder by converting the tetra(hydrocarbyl)borate to a compound having fewer than four carbon-to-boron bonds.

US 4,447,521 discloses imaging systems comprising a tetra(hydrocarbyl)borate and a bleachable dye that may be rendered desensitizable by the inclusion of a second bleachable dye which absorbs radiation in a different portion of the electromagnetic spectrum than the first bleachable dye.

US 4,450,227 relates to light sensitive systems comprising a tetra(hydrocarbyl)borate and a dye that may be used in the form of a dispersion, with the light sensitive borate and dye in one phase which is dispersed within a second phase.

US 4,772,530 describes a photohardenable composition comprising a free radical addition polymerizable or crosslinkable compound and an ionic dye-counter, compound, said compound being capable of absorbing actinic radiation and producing free radicals which initiate free radical polymerization or crosslinking of said compound; and photosensitive materials incorporating the same.

US 4,950,581 discloses the photopolymerizable composition containing a polymerizable compound having an ethyllenically unsaturated bond, a photopolymerization initiator and if necessary, a linear organic high molecular weight polymer. The photopolymerization initiator which is an organoboron compound comprises a combination of an alkali metal cation or a quaternary ammonium cation with a organoborane anion.

US 5,376,746, US 5,286,821 and US 5,143,884 relate to a two-part initiator system useful in adhesive compositions comprising in one part a stable organoborane/amine complex and in the second part an aldehyde destabilizer or activator. This initiator is particularly useful in elastomeric acrylic adhesive compositions and provides room temperature, relatively slow curing systems with good adhesive properties making them useful in applications where longer open times are required.

US 5,310,835 and US 5,106,928 describe a two-part initiator system useful in adhesive compositions comprising in one part a polymerizable acrylic monomers and an organoborane/amine complex and in the second part an organic acid destabilizer and optional acrylic polymer.

US 5,690,780 and US 2002/0028894 disclose polymerizable acrylic compositions which are particularly useful as adhesives wherein specific organoborane/amine complexes are used to initiate cure.

US 5,795,657 relate to organoborane/amine complexes comprising organoboranes and polyamines. The polyamine is the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine. The complexes are useful in systems for initiating the polymerization of acrylic monomers which systems further include a material reactive with the amine. Polymerizable acrylic monomer compositions useful in adhesive applications are also provided.

US 5,935,711 describe compositions comprising organoborane/amine complexes and aziridine-functional material to form polymerization initiator systems in acrylic-based polymerizable compositions useful in adhesive compositions for bonding low surface energy substrates.

US 5,952,409 discloses stain blocking compositions comprising a stain blocking material and an organoborane/amine complex.

US 5,990,036 and US 5,872,197 relate to systems for initiating polymerization of acrylic monomers comprising organoborane/amine complexes and bireactive decomplexers preferably comprising at least one free-radically polymerizable group and at least one amine-reactive group in the same molecule. The decomplexer is capable of forming a covalent bond with both the acrylic monomers and amine complex, resulting in a reduced level of mobile constituents.

US 6,027,813 and US 5,883,208 describe systems for initiating the polymerization of acrylic monomers comprising organoborane/amine complexes and decomplexers comprising at least one anhydride group. Adhesive compositions prepared from the initiator systems presented good adhesion on low surface energy substrates.

US 6,093,778, US 5,994,484 and US 6,008,308 disclose compositions comprising organoborane/amine complexes and polyols. The compositions can form a part of a polymerization initiator system that also includes polyisocyanate. The system can be used to initiate polymerization of acrylic monomer and to form a polyurethane/polyurea acrylic adhesive that has good adhesion to low surface energy substrates.

US 6,252,023 and WO 00/56779 relate to compositions comprising an organoborane/amine complex and 1,4-dioxo-2-butene functional material. The compositions can form a part of a polymerization initiator system that also includes a compound that is reactive with the amine position of the complex. The system can be used to initiate polymerization of acrylic monomer and to form an acrylic adhesive that exhibits good adhesion to low surface energy substrates.

US 6,248,846 describes polymerizable acrylic compositions comprising of at least one acrylic monomer, an effective amount of organoborane/amine complex and an effective amount of an acid for initiating polymerization of the acrylic monomer. The polymerizable acrylic compositions are useful for bonding low surface energy substrates.

US 2002/0028894 and US 2002/0033227 disclose a method polymerization and bonding two or more substrates together that comprises contacting the components of a composition comprising an organoborane/amine complex, one or more of monomers, oligomers, or polymers having olefinic unsaturation and optionally an effective amount of a compound which causes th complex to disassociate or heating the composition to a temperature at which the complex disassociates.

US 2002/0031607 relates to a method of modifying the surface of a low surface energy polymer by contacting the surface with a composition comprising an organoborane/amine complex, one or more of monomers, oligomers, or polymers having olefinic unsaturation and optionally an effective amount of a compound which causes th complex to disassociate or heating the composition to a temperature at which the complex disassociates.

WO 99/64475 describes initiator systems including both a complexed initiator (organoborane/amine complex) and a carboxylic acid decomplexer. Dicarboxylic acid, carboxylic acid esters, and monocarboxylic acid (preferably those comprising an alkyl group having at least nine carbon atoms fro low odor compositions) are useful as decomplexers in polymerizable compositions.

WO 99/64528 discloses low odor polymerizable compositions. The polymerizable compositions are useful in kits also comprising an aerobic initiator. Also disclosed are bonding compositions, polymerized compositions, coated substrates and methods of bonding in which the polymerizable compositions are especially useful.

WO 01/32716 relates to initiator systems compromising a complexed initiator comprising at least one of a complex of a complexing agent comprising at least one hydroxide (e.g. organoborane hydroxide complex) and an initiator or a complex of a complexing agent comprising at least one alkoxide (e.g. organoborane alkoxide complex) and an initiator or mixtures or combinations thereof; and a decomplexer.

WO 01/44311 describes an amine-organoborane complex wherein the organoborane is a trialkyl borane and the amine is an amine having an amidine structural component; an aliphatic heterocycle having at least one nitrogen in the heterocyclic ring wherein the heterocyclic compound may also contain one or more nitrogen atoms, oxygen atoms, sulfur atoms, or double bonds in the heterocycle; a primary amine which in addition has one or more hydrogen bond accepting group wherein there is at least two carbon atoms, preferably three, between the primary amine and the hydrogen bond accepting group, such that due to inter- or intramolecular interactions within the complex the strength of the B-N bond is increased; or a conjugated imine. Preferred hydrogen bond accepting groups include the following: a secondary amine, a tertiary amine, an ether, a halogen, a polyether group or a polyamine group. The complexes of the invention are used in polymerizable compositions, adhesive compositions and coatings compositions containing compounds having moieties which polymerize under free radical polymerization conditions.

WO 02/34851discloses the use of specific quaternary boron salts as initiators in polymerizable compositions and uses thereof for bonding low surface energy substrates.

WO 02/34852 relates to the use of metal alkyl borohydrides as initiators of polymerization, particularly in adhesive compositions for bonding a wide range of substrates including low surface energy substrates such as polyolefins. In particular, alkali metal trialkyl borohydrides are used, the alkali metal salt being selected from : lithium triethylborohydride, sodium triethylborohydride, potassium triethylborohydride, lithium tri-sec-butylborohydride, sodium tri-sec-butylborohydride,

potassium tri-sec-butylborohydride and lithium triethylborodeuteride and others less effective on low surface energy substrates such as lithium 9-borabicyclo [3.3.1]-nonane (9BBN) hydride, lithium thexylborohydride, lithium trisiamylborohydride and potassium trisiamylborohydride.

WO 03/035703 and WO 98/17694 describe (meth)acrylate based polymerizable compositions and adhesive systems prepared therefrom which include an aziridine-containing compound in a carrier material (diluent). The inventive compositions and adhesive systems are particularly well suited to bonding applications, which involve at least the bonding of one low energy surface (e.g. polyolefin, polyethylene, polypropylene, etc.).

WO 03/038006 discloses a two part composition for initiating cure of one or more polymerizable monomers which cure when exposed to free radicals comprising in one part an organoborane/amine complex and in the second part an isocyanate which is capable of decomplexing the organoborane complex wherein the ratio of amine nitrogen atoms to boron atoms is grater than 4.0:1.0.

WO 03/040151 relates to the use of internally blocked organoborates as initiators for free-radically polymerizable compositions useful in adhesive compositions.

WO 03/057791 describes metal salt modifiers for two-part bonding compositions useful in bonding low surface energy substrates. The metal salt modifiers modify the curing kinetics of the bonding composition.

US 4,538,920 disclose a multiple-barreled resin-dispensing device having a syringe, an exit conduit, a static mixing element, means for detachably coupling the inlet of the exit conduit to the outlet end of the syringe, and means for locating the static mixing element within the exit conduit to provide rotational alignment of the static mixing element relative to the syringe.

US 5,082,147 relates to an applicator that delivers from side by side chambers a two-part urethane polymer composition in which the diisocyanate is differentially reactive with two amine components of side B such that an initial, faster reaction with one amine keeps viscosity low while a second, slower reaction with the second amine builds viscosity to a self-supporting paste outside the applicator.

However, many problems remain, particularly regarding adhesive bond strength and composition stability. There remains an unmet need for stable adhesive compositions, which are capable of bonding low surface energy substrates. In particular, there remains the need for initiator systems for free radical polymerization which are safe to handle, are stable, and which can be used to cure polymerisable systems on demand.

The present invention provides a complex of an organoboron compound of the general formula

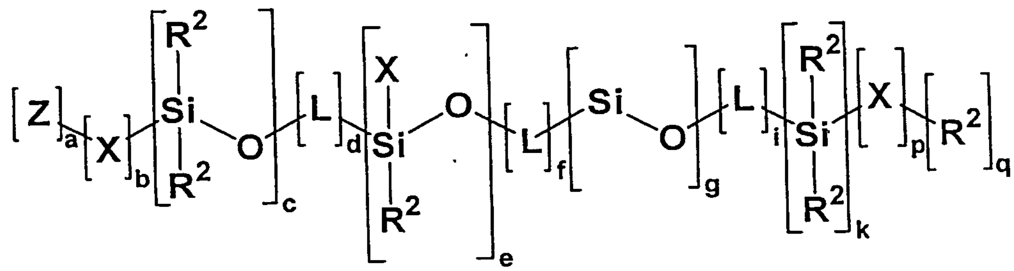
$$B(R^1)_3 \qquad (I)$$

in which each R^1 independently represents an alkyl, aryl, alkylaryl, arylalkyl, cycloalkyl, alkylcycloalkyl or cycloalkylalkyl group which may be unsubstituted or substituted by one or more of the same or different substituents selected from halogen atoms and alkoxy groups; with an organosilicon compound containing at least one primary, secondary and/or tertiary amino group.

Preferably an alkyl or alkoxy group present in R^1 has from 1 to 10, preferably 1 to 6, especially 1 to 4, carbon atoms, and preferably any aryl moiety is a phenyl group. A cycloalkyl moiety preferably has from 5 to 7 carbon atoms. Preferred halogen atoms are chlorine and fluorine atoms.

Preferably each R^1 independently represents a C_{1-4} alkyl group. Most preferably the compound of formula I is tri-*n*-butylborane, tri-*t*-butylborane, triisopropylborane or, especially, triethylborane.

The organosilicon compound may be based on a silane, silicone, silica gel, silazane, silatrane or silsesquioxane. Particularly suitable compounds may be represented by the following general formulae II and V:

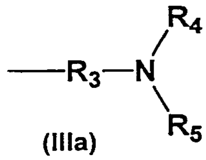


(II)

in which:
a, **q**, are independently equal to 0 or 1;
b, **c**, **d**, **e**, **f**, **g**, **i**, **k**, **p**, are independently equal to or higher than 0;
(**a**, **c**, **e**, **g**, **k**, cannot be all equal to 0 at the same time. At least one of them should be higher than 0 and at least one of the **b**, **d**, **f**, **i**, **p** should be equal to or higher than 1).

each R^2 independently represents a hydrogen atom or a hydroxyl group or an alkyl (e.g. isopropyl, isobutyl, isooctyl, propylisobutyl, etc.), halogen alkyl, glycidyl alkyl, acrylalkyl, (meth)acrylalkyl, alkoxy, alkoxyalkyl, alkenyl, cycloalkyl (e.g. cyclohexyl, propylcyclohexyl, etc.), aryl, alkyloxyaryl, aryloxyalkyl or alkyloxycycloalkyl group, each of which may be optionally substituted by one or more primary, secondary or tertiary amino groups and/or other functional groups such as hydroxyls, carbonyls; and
each X (which can be monovalent or divalent depending on the values of a, c, d, e, f, g, i, k, and q) independently represents a group of the general formulae (III) and (IV):

monovalent X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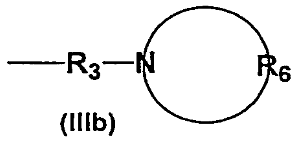
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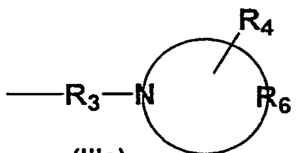
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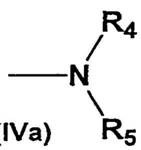
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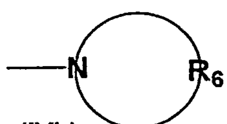
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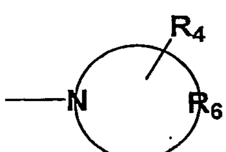
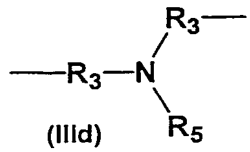

(IVc)

divalent X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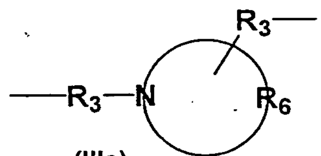
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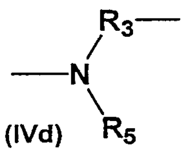
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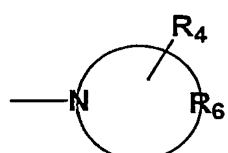
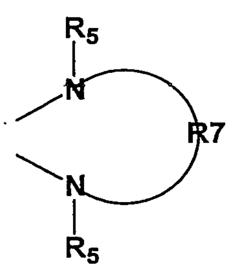

(IVe)


(IVf)

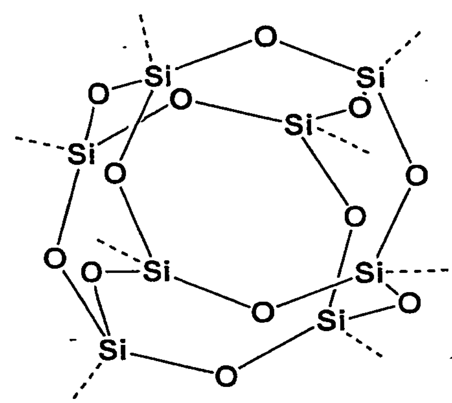
in which R^3 represents an alkylene, alkenyl, phenylene or cycloalkylene group; and each of R^4 and R^5 independently represents a hydrogen atom, a hydroxyl group, or an alkyl, aryl, silylalkyl, silylaryl, cycloalkyl, arylalkyl, alkylaryl, cycloalkylalkyl, alkylcycloalkyl, eterocyclic (saturated or unsaturated), phenyl (Ph-), phenoxy (Ph-O-), or Ph-(C=O)- group each of which may be optionally substituted by one or more primary, secondary or tertiary amino groups and/or other functional groups such as

hydroxyls, carbonyls, etc., R^4 and R^5 can independently be also R^2, R^6 can be a "cyclic" group that means a closed ring hydrocarbon group that is classified as an alicyclic group, aromatic group, or eterocyclic (saturated or unsaturated) group and each one of them can be mono-, di-, tri-, tetra-, penta-substituted by R^3 or R^4 groups (structures IIIc, IIIe, IVc and IVe described only the mono-substituted derivatives). X can also contain organic groups or organic linking groups can include heteroatoms (e.g. O, S, Si atoms) such as in the case of heterocyclic compounds as well as functional groups (e.g. carbonyl, hydroxyl groups, etc).

R^7 can be a "cyclic" of the structure $-Si(R^2)-[Si(R^2)_2-NH-]_n-Si(R^2)-$, where n is equal to or higher than 1.

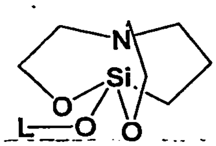
in which L represents:
A monovalent or divalent (depending on the values of the a, b, c, e, g, k, p and q) group and can be independently selected from any of the groups representing the X group or it can also be R^2 or R^3 or R^5 or R^4 or R^6 or R^7 or any polymeric/oligomeric organic mono- or di-radical.

in which Z represents:



where <u>every</u> silicon atom forms a bond (represented by the dashed lines on the above drawing) with either X or R^2 or R^4 or R^5 and at least one silicon atom must be bonded with one X.

The general formula II does not include silatranes, which can be represented by the following general formula V:



(V)

in which L (only monovalent in these compounds) represents exactly the same things as mentioned before.

In the organosilicon compound, and elsewhere throughout this specification and claims except where otherwise stated, any alkyl moiety preferably has 1 to 10, preferably 1 to 6, and most preferably 1 to 4 carbon atoms; an alkyl moiety may for example be a methyl group; any aryl group is preferably a phenyl group; and any cycloalkyl group preferably has from 5 to 8 carbon atoms.

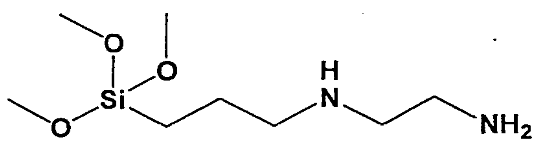
High molecular weight silicon compounds may be used, for example compounds having a molecular weight up to 6,000,000. In high molecular weight compounds, m plus n may for example be up to 70,000.

Typically the organosilicon compound may have the formula derived from the general formula II for b=1, c=1, q=1 and a, d, e, f, g, i, k, p, q are all independently equal to 0 and where X and R^2 groups are as defined here before.

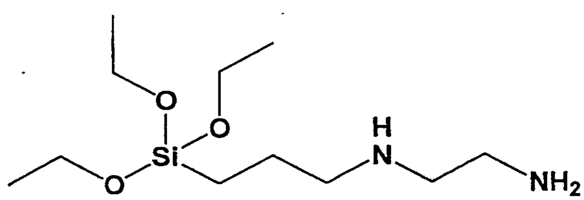
Typically the organosilicon compound may have the formula derived from the general formula II for b=1, c>1, e>1, k=1, p=1 and a, d, f, g, i, q are all independently equal to 0 and where X and R^2 groups are as defined here before.

Typically the organosilicon compound may have the formula derived from the general formula II for a=1, b=1 and c, d; e, f, g, i, k, p, q are all independently equal to 0 and where X group is as defined here before.

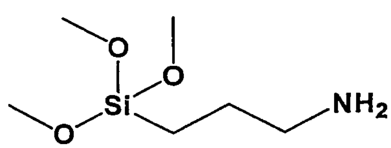
One preferred group of silicon compounds described by the general formula II, are silanes, which contain primary or secondary or tertiary amino groups or combinations thereof. Examples of suitable silanes are represented by the following formulae:



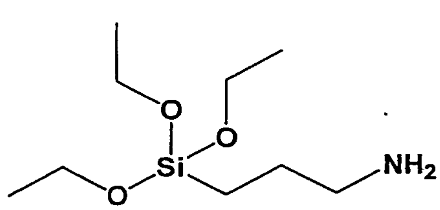
3-(2-aminoethylamino)propyltrimethoxy silane



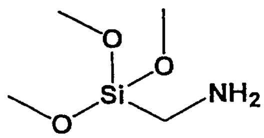
3-(2-aminoethylamino)propyltriethoxy silane



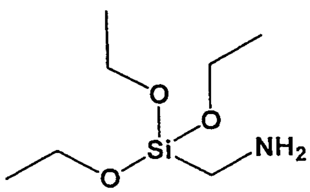
(3-aminopropyl)trimethoxy silane



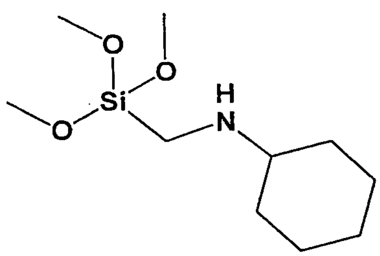
(3-aminopropyl)triethoxy silane



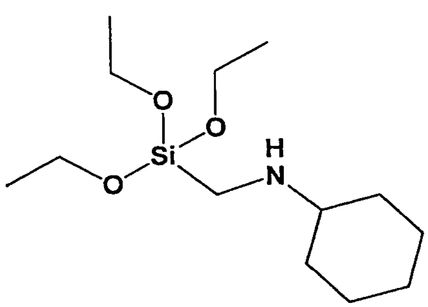
(aminomethyl)trimethoxy silane



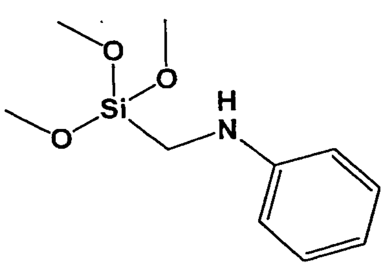
(aminomethyl)triethoxy silane



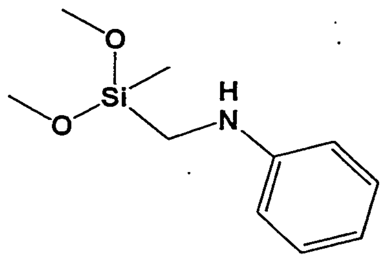
(N-cyclohexylaminomethyl)trimethoxy silane



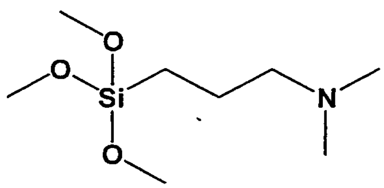
(N-cyclohexylaminomethyl)triethoxy silane



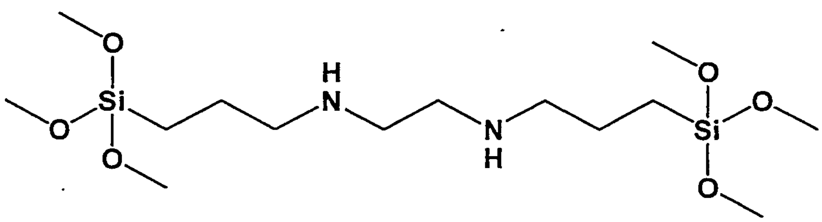
(N-phenylaminomethyl)trimethoxysilane



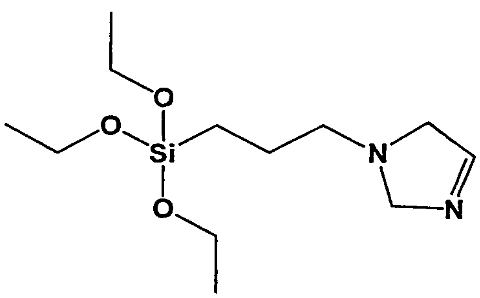
(N-phenylaminomethyl)methyldimethoxysilane



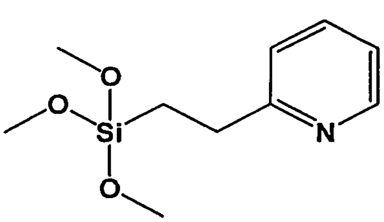
(N,N-dimethylaminopropyl)trimethoxysilane



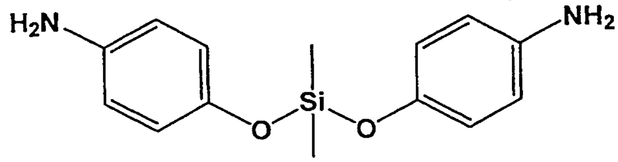
Bis[(3-trimethoxysilyl)propyl]ethylenediamine



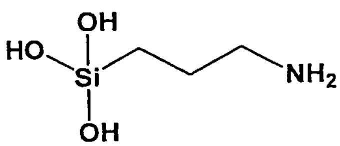
N-(3-triethoxysilylpropyl)4,5-dihydroimidazole



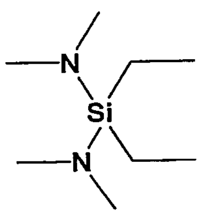
2-(trimethoxysilylethyl)pyridine



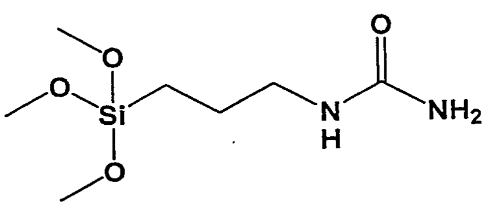
Bis(p-aminophenoxy)dimethylsilane



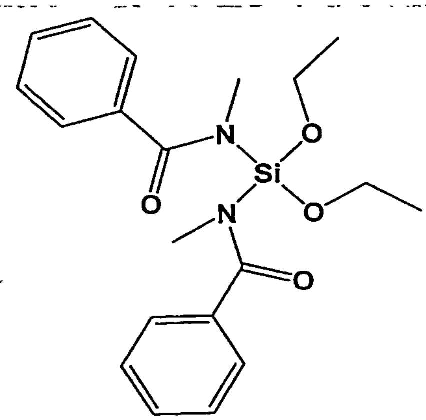
·Aminopropyltrihydroxysilane



Bis(dimethylamino)diethylsilane

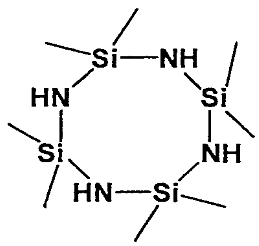


Ureidopropyltrimethoxysilane

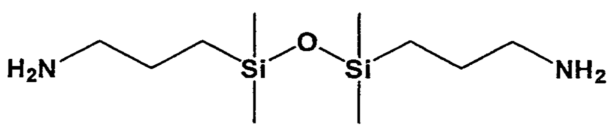


Bis(N-methylbenzamido)ethoxymethylsilane

Other compounds that are described by the general formula II are:

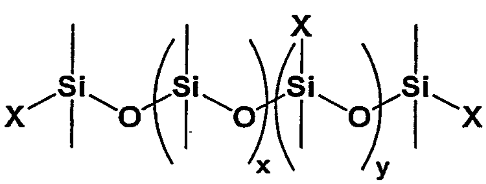


Octamethylcyclotetrasilazane



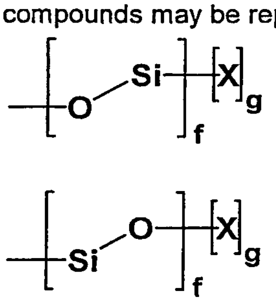
1,3-Bis(3-aminopropyl)tetramethyldisiloxane

The organosilicon compound of the general formula (II) may be an organofunctional silicone fluid. Such compounds may be represented by the following formula, which may contain one or more organic groups X in the positions shown:



in which x and y are integers.

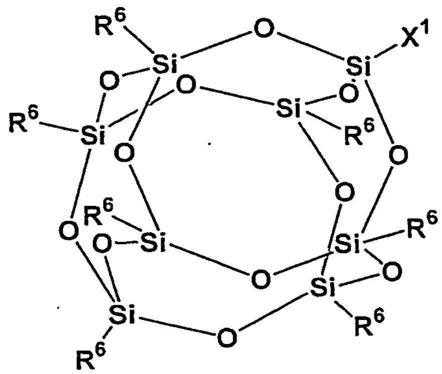
The organosilicon compound of the general formula (II) may be an organofunctional silica gel. Such compounds may be represented by the following formula,



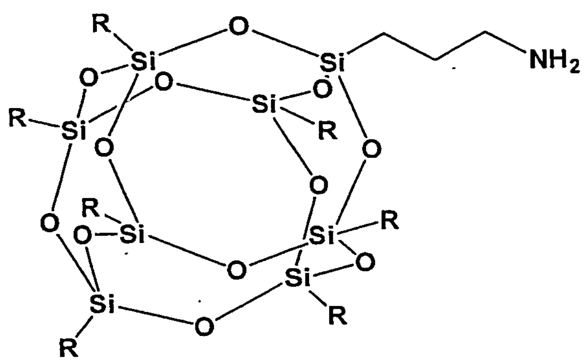
in which f and g are each one higher than 0.

Alternatively, the organosilicon compound may be a so-called Polyhedral Oligomeric Polysilsesquioxane (POSS) bearing at least one organic group X. POSS materials are classified as nanostructured chemicals, and are the smallest particles of silica possible. However, unlike silica, silicones, or fillers, each POSS molecule contains non-reactive organic functionalities for solubility and compatibilization of the POSS nanostructure with polymers, biological systems, and surfaces. In addition, POSS nanostructured chemicals can contain one or more covalently bonded reactive

functionalities suitable for polymerization, grafting, surface bonding, or other transformations. Typical generic chemical structure is as follows:

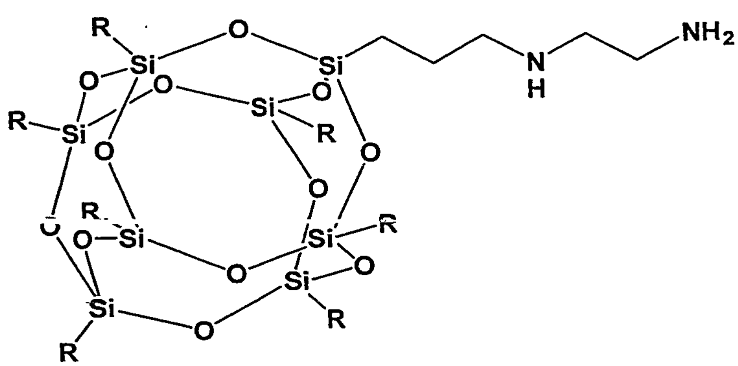


where the X^1 is the same as X; R^6 is the same as R^2 or R^2 or R^4 or R^5 or X. Typical such compounds finding utility in the present invention include:



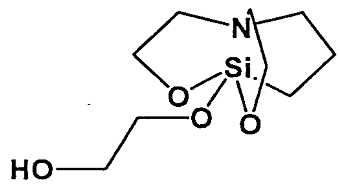
where R is aminopropylcyclohexyl, aminopropylisobutyl, or aminopropylisooctyl

and



where R is aminoethylaminopropylcyclohexyl or aminoethylaminopropylisobutyl.

A typical example of a compound described by the general formula V is the following:



Hydroxyethoxysilatrane

The compounds that can be used in forming complexes with substances of the general formula (I) may also be a mixture of at least two of the above-mentioned typical organosilicon compounds.

The complexes of the present invention may be prepared for example by contacting a solution of the organoborane compound of the general formula (I) with the organosilicon compounds of the general formula II, suitably under an inert atmosphere, with cooling if required.

In the complexes according to this invention the ratio of boron atom (organoborane) to nitrogen atom (decomplexing agent) can be as low as 0.01:1 (ratio B:N), preferably higher than 0.3:1 and most preferably 1:1. In certain of the complexing agents described by the general formula II, this ratio can be higher than 1:1 (e.g. 3:1, 7:1, 10:1, 21:1, etc.) depending on the molecular weight of the these complexing agents. The higher the molecular weight, the more this ratio can deviate from the 1:1 towards higher number of boron atoms to 1 nitrogen atom.

The complexes according to the present invention are air stable and can be utilized as polymerisation initiators for radically polymerisable monomers or oligomers, and accordingly the present invention provides a polymerisable composition which comprises a complex according to the invention and at least one radically polymerisable monomer and/or oligomer. Such compositions find application as, for example, paints, coatings, sealants, inks, primers, stain blocking compositions, mouldings and, especially, adhesives. Such materials, especially when used in adhesive applications, are commonly formulated as two-part products in which the two parts are mixed together as required to initiate curing. Accordingly, the invention also provides a two-part polymerisable composition, in which a first part comprises a complex according to the invention and a second part comprises at least one radically polymerisable monomer and/or oligomers. The invention further provides a method of adhesively bonding two substrates together, which comprises applying a polymerisable composition according to the invention (which may involve mixing together the two parts of a two part polymerisable composition) to a first substrate, positioning a second substrate (that may or may not be coated with the polymerizable product) in contact with the first substrate via said product, and allowing or causing the product to cure. Although substrates of surface energy higher than 40-45 mJ/m^2 can be bonded (e.g. stainless steel, iron, aluminium, copper, tin, lead, glass, polypropylene oxide, polyethersulfone, etc.), the invention is particularly useful for adhesively bonding together low surface energy substrates or in cross bonding a low surface energy substrate with different substrates (e.g. metals). Thus, preferably at least one substrate is a low surface energy substrate. A low surface energy substrate generally has a surface energy of less than 50 mJ/m^2, less than 40 mJ/m^2 or even less than 35 mJ/m^2. Included among the recognized low surface energy substrates are materials like polyethylene, polypropylene, copolymers of a-olefins, and fluorinated polymers such as polytetrafluoroethylene. Other polymers that can be bonded include polycarbonate, poly(methyl methacrylate), acrylonitrile-butadiene-styrene as well as other polymers and plastics with higher surface energy. However the invention is not limited to bonding of low surface energy materials. The compositions may be used to bond any thermoplastics, thermosets as well as wood, composites, ceramics, glass, concrete, and metals.

The invention further provides the use of a complex according to the invention as an initiator for the polymerisation of a radically polymerisable monomer or oligomer.

Preferably the second part of a two-part polymerisable composition according to the invention also includes a decomplexing agent capable of releasing the organoborane compound from the complex such that, on mixing of the two parts, the decomplexing agent reacts with the organosilicon-based organoborane compound, liberating as a result the organoborane compound. The organoborane compound in turn initiates polymerisation. Any compound capable of releasing the boron compound from the complex may be used as decomplexing agent. Examples of such compounds can be

found in WO 99/64475, WO 00/56779. Preferable examples include acids (Lewis acids i.e. $SnCl_4$, $TiCl_4$ and the like, Brönsted acids [e.g. mono- or poly-carboxylic acids saturated or unsaturated], HCl, H2SO4, H_3PO_4, phosphonic acid, phosphinic acid, silicic acid and the like), mono- or poly-carboxylic acid esters (saturated or unsaturated), anhydrides, isocyanates, cyclocarbonates, aldehydes, acid chlorides, sulphonyl chlorides, and epoxies. The decomplexing agent according to the present investigation is employed in an effective amount and can also be a mixture of at least two decomplexers; that is an amount effective to promote polymerization by liberating organoborane from the complex, but without materially adversely affecting the properties of the ultimate polymerized composition. If larger amounts of these decomplexers are employed, this may speed-up polymerization in such an extend that in the case of adhesives, the resulting materials may demonstrate inadequate adhesion to low surface energy surfaces. However, a reduced amount of these decomplexers may be helpful in slowing down the rate of polymerization if it is otherwise fast. Within these parameters, the ratio of the equivalents of the decomplexer to those of the organoborane can be from 0.01 to 5:1 (ratio decomplexer: organoborane), more preferably from 0.05 to 4:1 and most preferably from 0.1:1 to 2:1.

In an alternative embodiment, the polymerisation reaction may be initiated by supplying an appropriate form of energy to the system [the initiator (organoborane/organosilicon complex) may or may not be in a separate part to the polymerizable monomers] comprising the polymerisable composition, the energy being sufficient to release the boron compound from the complex. Suitably the energy is supplied by heating, or by the application of actinic radiation or by electromagnetic radiation or by magnetic radiation, electrical current, ultrasounds, ultraviolet radiation combinations thereof or any other means that result to the aforementioned specie of radiation or heat. This, in the case of adhesive formulations permits the development of one-component adhesives the curing of which can be triggered by any of the aforementioned energy sources.

The polymerization rate which is a crucial parameter for the effectiveness of the compositions described in this embodiment, can be tuned according to the type of the applicator i.e. a faster polymerization rate could be accommodated by using a high-speed automated industrial adhesive applicator whilst a lower polymerization may be desirable for applications where the adhesive needs to be applied either by a hand applicator or to be mixed manually. Preferably a composition according to the invention contains sufficient complex to provide 0.001 to 10%w, preferably 0.002 to 7.0%w, and most preferably 0.003 to 5.0% of boron, based on the total weight of the composition.

In another aspect of the present invention, the organoborane/organosilicon compound complex can be used as a primer. In this case, a composition comprising a novel complex according to the invention is applied to the surface of a substrate, typically a low surface energy substrate. In a second step, a composition comprising a radically polymerisable monomer or oligomer is applied to the thus-primed surface, followed by application of a second substrate that is or is not similarly treated.

In yet another aspect, a composition comprising a complex according to the invention together with a radically polymerisable monomer or oligomer is applied to the surface of a substrate, typically a low surface energy substrate and left to cure, which renders the substrate bondable with conventional adhesives.

In another aspect, the newly prepared complexes can be used in stain blocking compositions comprising a stain blocking material as those described in essence in US 5,952,409 (e.g. sulfonated aromatic polymers, polymers that are derived from at least one or more (a- and/or b-substituted) acrylic acid monomers and hydrolyzed copolymers of at least one or more ethyllenically unsaturated monomers and maleic anhydride, blends of at least two or more of these polymers, reaction products of at least two or more of the monomers from which these polymers may be derived and at least one or more of the polymers and materials obtained by polymerizing at least one or more of the monomers in the presence of one or more of the polymers, to mention some).

The compositions of the invention may also, if required, include a mixture of two or more organosilicon organoborane complexes in combination with a solvent and/or reactive or non-reactive diluent.

The polymerizable compositions of the invention may be used in a wide variety of ways, including as sealants, coatings, inks, primers, to modify the surface of polymers and injection molding resins.

They may also be used as matrix resins in conjunction with glass and metal fiber mats such as in resin transfer molding operations. They may further be used as encapsulants and potting compounds such as in the manufacture of electrical components and printed circuit boards. Quite desirably, they provide polymerizable adhesive compositions that can bond a diverse myriad of substrates, including polymers, wood, ceramics, concrete, glass and metals. Another desirable related application is their use in promoting adhesion of paints to low surface energy substrates such as polyethylene, polypropylene, polyethyleneterephthalate and polytetrafluoroethylene and their co-polymers. In this embodiment the composition may be coated onto the surface of the substrate to modify the surface to enhance the adhesion of the final coating to the surface of the substrate or added to the coating itself.

The compositions of the invention can be used in coating applications. In such applications the composition may further comprise a diluent. The coating may further contain additives well known to those skilled in the art for the use in coatings such as pigments to color the coating, inhibitors and UV stabilizers. The compositions may also be applied as powder coatings and may contain the additives well known to those skilled in the art for use in powder coatings.

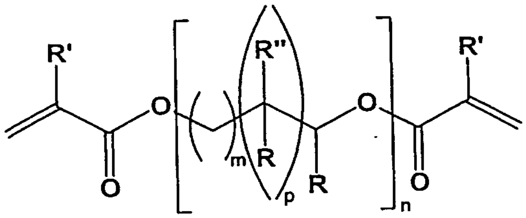
The compositions of the invention can also be used to modify the surface of a polymeric molded part, extruded film or contoured object. Compositions of the invention can also be used to change the functionality of a polymer particle/article by surface grafting of polymer chains onto the unmodified plastic surface.

Polymerizable Monomers/Oligomers

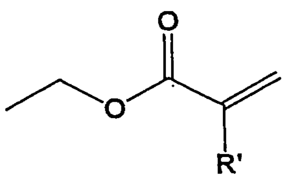
The invention is adapted to a variety of polymerizable compositions and includes any monomers, oligomers, polymers or mixtures thereof which contain olefinic unsaturation (characterized by the presence of a >C=C< group), which can be polymerized by free radical polymerization caused by the organoborane liberated from the organosilicone-based organoborane complex. Such compounds are well known in the art. U.S. Pat. 3,275,611, U.S. Pat. 5,690,780, U.S. Pat. 5,795,657, U.S. Pat. 5,872,197, U.S. Pat. 5,286,821, U.S. Pat. 5,681,910, WO 03/040151, WO 00/56779, WO 99/64475, WO 03/057791, to mention some as well as the literature (patents, papers, books, etc.) mentioned by them, provide a description of such compounds. Among preferred classes of compounds containing olefinic unsaturation are for example ethylene, propylene, butylenes, isobutylene, 1-octene, 1-dodecene, 1-heptadecene, 1-eicosene; vinyl compounds such as styrene, vinyl pyridine, 5-methyl-2-vinylpyridine, vinyl naphthylene, alpha methylstyrene; vinyl and vinylidiene halides; acrylonitrile and methacrylonitrile; vinyl acetate and vinyl propionate; vinyl oxyethanol; vinyl trimethylacetate; vinyl hexanoate; vinyl laurate; vinyl chloroacetate; vinyl stareate; methyl vinyl ketone; vinyl isobutyl ether; vinyl ethyl ether; compounds that have a plurality of ethylenic bonds such as those having conjugated double bonds such as butadiene, 2-chlorobutadiene and isoprene; acrylates and methacrylates such as methyl methacrylate, methyl acrylate, butyl methacrylate, t-butyl methacrylate, 2-ethylhexyacrylate, 2-ethylhexylmethacrylate, ethyl acrylate, isobornyl methacrylate, isobornyl acrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, tetrahydrofurfuryl methacrylate, acrylamide, n-methyl acrylamide, and other similar acrylate or methacrylate containing monomers that can be mono and/or poly-functional and can contain apart from hydroxyl, amide and cyano groups, chloro and silane substituents. Also useful for the class of acrylate tipped polyurethane prepolymers available commercially from several sources and prepared by reacting an isocyanate reactive acrylate monomer, oligomer or polymer such as hydroxyl acrylate, with an isocyanate functional prepolymer.

Certain acrylic or methacrylic monomer combinations have been found to be particularly advantageous in providing polymerizable compositions having less odor. Such monomer combinations preferably comprise about 10-90% w/w on total weight of the monomer blend, tetrahydrofurfuryl methacrylate; 5-80% w/w on total weight of the monomer blend, of one or more monomers selected from the group consisting of 2-ethylhexyl methacrylate, 2-ethylhexyl methacrylate, 2-ethoxyethyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, isooctyl acrylate and isooctyl methacrylate; and 0-70% w/w on total weight of the monomer blend, of one or more monomers selected from the group consisting of isobutyl methacrylate, n-butyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl methacrylate, isobornyl methacrylate, isodecyl methacrylate and isodecyl acrylate.

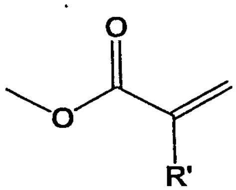
Another class of polymerizable monomers useful in the compositions of the present invention correspond to the following general formula



wherein R is selected from the group consisting of hydrogen methyl, ethyl, $-CH_2OH$, and

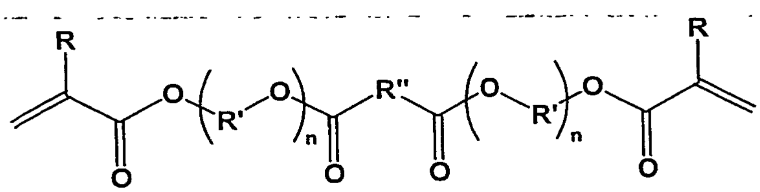


R' is selected from the group consisting of chlorine, methyl and ethyl; R" is selected from the group consisting of hydrogen, hydroxyl and

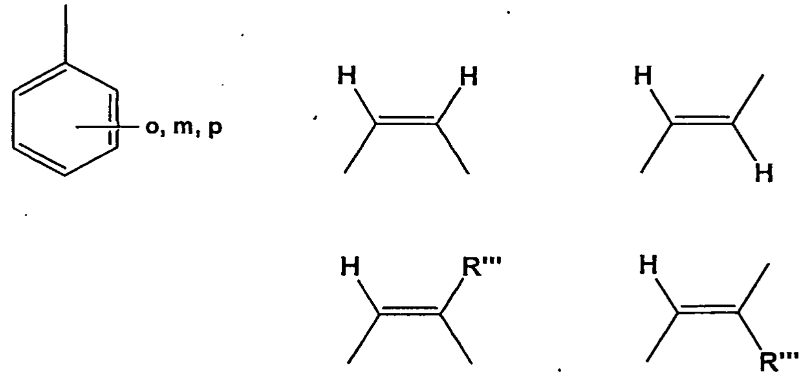


m is an integer equal to at least 1, e.g. from 1 to 8 or higher and preferably from 1 to 4 inclusive; n is an integer equal to at least 1, e.g. from 1 to 20 or more; and p is 0 or 1. Monomers that come within the above general formula include for example, ethylene glycol dimethacrylate, ethylene glycol diacrylates, polyethylene glycol diacrylates, tetraethylene glycol dimethacrylate, diglycerol diacrylates, diethylene glycol dimethacrylate, pentaerythritol triacrylate, trimethylpropane trimethacrylate and other polyether diacrylates and dimethacrylates. This class of materials is described in essence in U.S. Pat. 5,106,928 and U.S. Pat. 3,043,820.

Another class of polymerizable monomers useful in the present compositions corresponds to the following general formula:

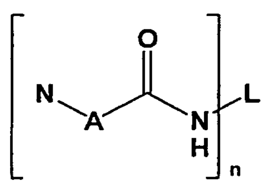


wherein R represents hydrogen, chlorine, methyl, or ethyl; R' represents alkylene with 2-6 carbon atoms; and R" represents $(CH_2)_m$ in which m is an integer of from 0 to 8, or



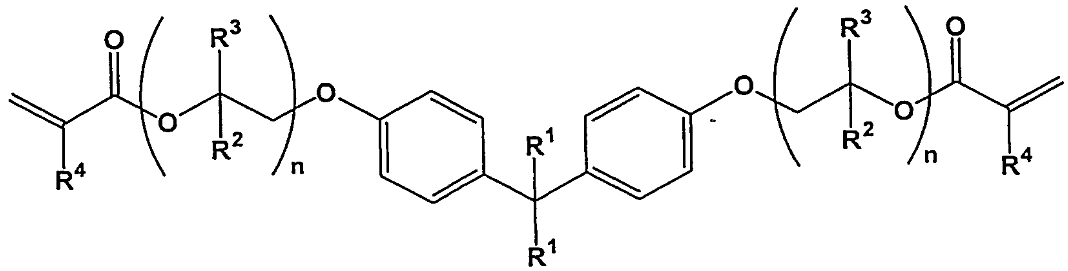
n represents an integer of from 1 to 4 and R''' is methyl. Typical monomers of this class include, for example dimethylacrylate of bis(ethylene glycol) adipate, dimethylacrylate of bis(ethylene glycol)maleate, dimethylacrylate of bis(ethylene glycol) phthalate, dimethylacrylate of bis(tetraethylene glycol) phthalate, dimethylacrylate of bis(tetraethylene glycol) sebacate, dimethylacrylates of bis(tetraethylene glycol) maleate and the diacrylates and chloroacrylates corresponding to said dimethacrylates and the like. This class of polymerizable monomers are described in essence in U.S. Pat. 5,106,928 and U.S. Pat. 3,457,212.

Another useful class of polymerizable monomers in the compositions of the present invention include monomers which are isocyanate-hydroxyacrylate or isocyanate-aminoacrylate reaction products which may be characterized as acrylate terminated polyurethanes and polyureides or polyureas. These monomers correspond to the following general formula:



where A is selected from the group consisting of –O- and >N-R^7, and R^7 is a member selected from the group consisting of hydrogen and lower alkyl of 1 to 7 carbon atoms; N represents the organic residue of an active hydrogen containing acrylic ester wherein the active hydrogen has been removed, the ester being hydroxy or amino substituted on the alkyl portion thereof and the methyl, ethyl, and chlorine homologs thereof; n is an integer from 1 to 6 inclusive; L is a mono- or polyvalent organic radical selected from the group consisting of alkyl, alkylene, alkenyl, cycloalkyl, cycloalkylene, aryl, arylalkyl, alkylaryl, poly(oxyalkylene), poly(carboalkoxyalkylene) and heterocyclic radicals both substituted and unsubstituted. Typical monomers of this class include the reaction product of mono- or poly-isocyanate, for example, toluene diisocyanate, with an acrylate ester containing a hydroxy or an amino group in the non-acrylate portion thereof, for example, hydroxyethyl methacrylate. The above class of monomers are described in essence in U.S. Pat. 5,106,928 and U.S. Pat. 3,426,988.

Another class of monomers useful herein are the mono- and poly-acrylate and methacrylate esters of bisphenol-type compounds many of which are widely available. These compounds can be described by the following formula:

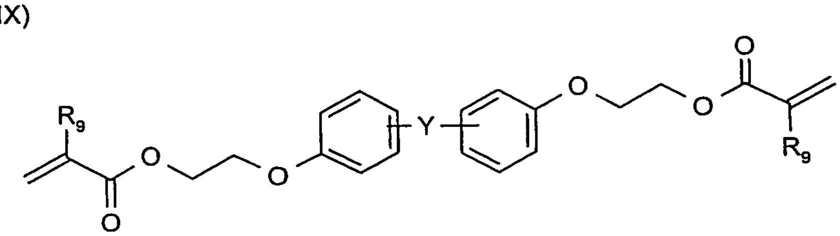


where R^1 is methyl, ethyl, carboxyalkyl or hydrogen; R^2 is hydrogen, methyl or ethyl; R^3 is hydrogen, methyl or hydrogen; R^4 is hydrogen, chlorine, methyl or ethyl, and n is an integer having a value of 0 to 8. Representative monomers of the above-described class include: dimethacrylate and diacrylates esters of 4,4'-bis-hydroxyethoxy-bisphenol A, dimethacrylate and diacrylates esters of bisphenol A, etc. These monomers are essentially described in Japanese Patent 70-15640 and in WO 5,106,928.

The (meth)acrylates used herein are known compounds and some are commercially available, for example from the SARTOMER Company under product designations such as SR®203, SR®295, SR®350, SR®351, SR®367, SR®399, SR®444, SR®454 or SR®9041.

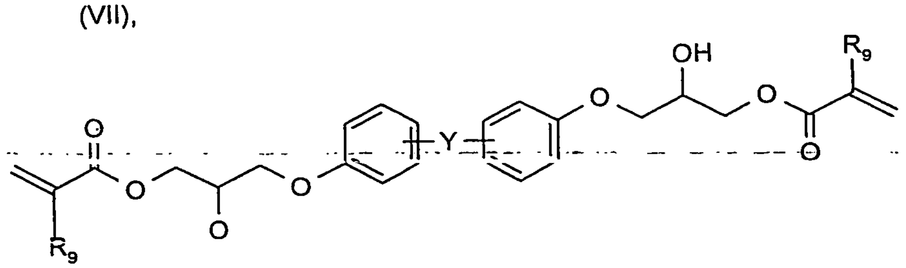
Suitable examples of di(meth)acrylates are the di(meth)acrylates of cycloaliphatic or aromatic diols such as 1,4-dihydroxymethylcyclohexane, 2,2-bis(4-hydroxy-cyclohexyl)propane, bis(4-hydroxycyclohexyl)methane, hydroquinone, 4,4'-dihydroxybi-phenyl, Bisphenol A, Bisphenol F, bisphenol S, ethoxylated or propoxylated Bisphenol A, ethoxylated or propoxylated Bisphenol F or ethoxylated or propoxylated bisphenol S. Di(meth)acrylates of this kind are known and some are commercially available.

Other di(meth)acrylates which can be employed are compounds of the formulae (VI), (VII), (VIII) or (IX)

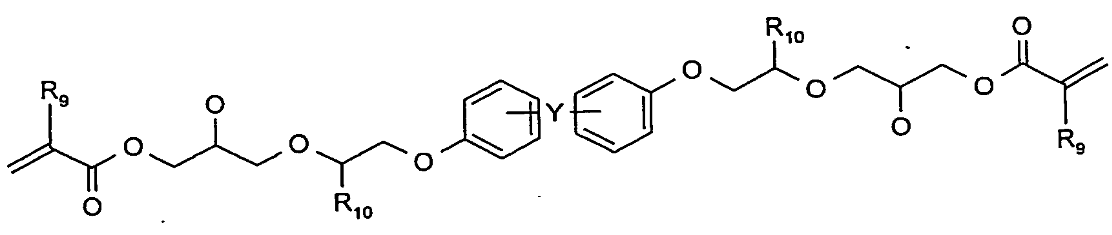


(VI),

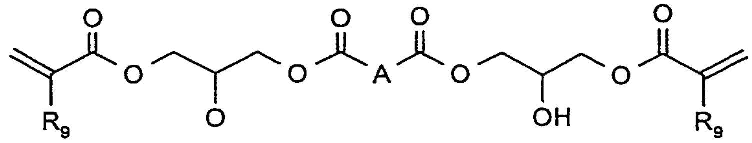
(VII),



(VIII),



(VIII)



(IX)

in which

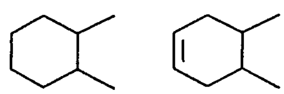
R_9 is a hydrogen atom or methyl,

Y is a direct bond, C_1-C_6alkylene, -S-, -O-, -SO-, $-SO_2-$ or -CO-,

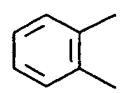
R_{10} is a C_1-C_8alkyl group, a phenyl group which is unsubstituted or substituted by one or more C_1-C_4alkyl groups, hydroxyl groups or halogen atoms, or is a radical of the formula $-CH_2-OR_{11}$ in which

R_{11} is a C_1-C_8alkyl group or phenyl group, and

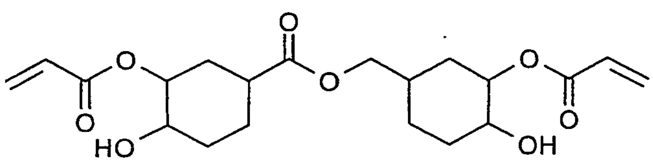
A is an alkylene group or a group of the formula



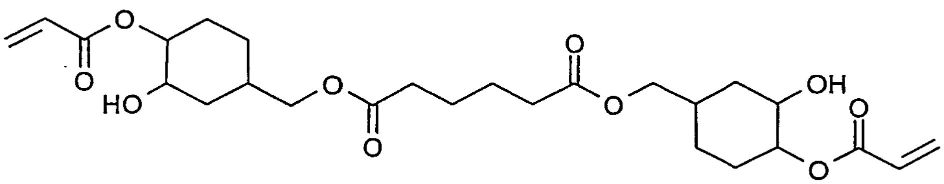
, or



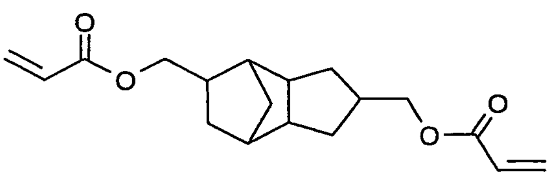
Further examples of possible di(meth)acrylates are compounds of the formulae (X), (XI), (XII) and (XIII)



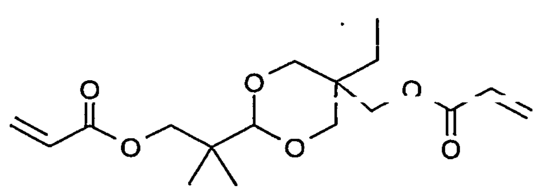
(X),



(XI),



(XII),



(XIII)

These compounds of the formulae (VI) to (XIII) are known and some are commercially available. Their preparation is also described in EP-A-0 646 580.

Examples of commercially available products of these polyfunctional monomers are KAYARAD R-526, HDDA, NPGDA, TPGDA, MANDA, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, THE-330, DPHA-2H, DPHA-2C, DPHA-21, D-310, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, TPA-320, TPA-330, RP-1040, R-011, R-300, R-205 (Nippon Kayaku Co., Ltd.), Aronix M-210, M-220, M-233, M-240, M-215, M- 305, M-309, M-310, M-315, M-325, M-400, M-6200, M-6400 (Toagosei Chemical Industry Co, Ltd.), Light acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA, DCP-A (Kyoeisha Chemical Industry Co., Ltd.), New Frontier BPE-4, TEICA, BR-42M, GX-8345 (Daichi Kogyo Seiyaku Co., Ltd.), ASF-400 (Nippon Steel

Chemical Co.), Ripoxy SP-1506, SP-1507, SP-1509, VR-77, SP-4010, SP-4060 (Showa Highpolymer Co., Ltd.), NK Ester A-BPE-4 (Shin-Nakamura Chemical Industry Co., Ltd.), SA-1002 (Mitsubishi Chemical Co., Ltd.), Viscoat-195, Viscoat-230, Viscoat-260, Viscoat-310, Viscoat-214HP, Viscoat-295, Viscoat-300, Viscoat-360, Viscoat-GPT, Viscoat-400, Viscoat-700, Viscoat-540, Viscoat-3000, Viscoat-3700 (Osaka Organic Chemical Industry Co., Ltd.).

Other (meth)acrylate compositions are those in which the free radically curable component contains a tri(meth)acrylate or a penta(meth)acrylate. Examples of suitable aromatic tri(meth)acrylates are the reaction products of triglycidyl ethers of trihydric phenols and phenol or cresol novolaks containing three hydroxyl groups, with (meth)acrylic acid.

Vinyl ethers that can be used as a radically polymerisable compound in the present invention include ethyl vinylether, n-propyl vinylether, isopropyl vinylether, n-butyl vinylether, isobutyl vinylether, octadecyl vinylether, cyclohexyl vinylether, butanediol divinylether, cyclohexanedimethanol divinylether, diethyleneglycol divinylether, triethyleneglycol divinylether, tert-butyl vinylether, tert-amyl vinylether, ethylhexyl vinylether, dodecyl vinylether, ethyleneglycol divinylether, ethylene- glycolbutyl vinylether, hexanediol divinylether, triethyleneglycol methylvinylether, tetraethyleneglycol divinylether, trimethylolpropane trivinylether, aminopropyl vinylether, diethylaminoethyl vinylether, ethylene glycol divinyl ether, polyalkylene glycol divinyl ether, alkyl vinyl ether and 3,4-dihydropyran-2-methyl 3,4-dihydropyran-2-carboxylate. Commercial vinyl ethers include the Pluriol-E200 divinyl ether (PEG200-DVE), poly-THF290 divinylether (PTHF290-DVE) and polyethyleneglycol-520 methyl vinylether (MPEG500-VE) all of BASF Corp.

Hydroxy-functionalised mono(poly)vinylethers include polyalkyleneglycol monovinylethers, polyalkylene alcohol-terminated polyvinylethers, butanediol monovinylether, cyclohexanedimethanol monovinylether, ethyleneglycol monovinylether, hexanediol monovinylether, diethyleneglycol monovinylether.

Another class of vinyl ethers that are suitable for inclusion are all those included in US 5,506,087, which is incorporated herein by reference. More preferred are aromatic or alicyclic vinyl ethers. As an example, commercial vinylethers include Vectomer 4010, Vectomer 5015, Vectomer 4020, Vectomer 21010 and Vectomer 2020 of Allied Signal Corp., Morristown, NJ. Most preferred are Vectomer 4010 and Vectomer 5015.

Another class of polymerisable monomers includes vinyl-functionalized silicones (vinylsiloxanes), vinyl functionalized silatranes, vinyl functionalized alpha- or gamma-silanes and vinyl functionalized POSS compounds. To mention some, typical examples of vinylsiloxanes are: bis(m-allylphenyldimethylsilyloctyl)tetramethyldisiloxane (SIB1021.0) and the like, supplied by ABCR GmbH & Co. KG. and X-22-164B, X-22-164C, X-22-5002, X22-174D (modified silicone fluids) and the like supplied by Shin-Etsu Chemical Co., Ltd.. Typical example of vinyl functionalized silatranes is the methacryloxypropylsilatrane (SIM6487.1) and the like supplied by ABCR GmbH & Co. KG. Typical examples of vinyl functionalized α- or γ-silanes: styrylethyltrimethoxysilane (SIS6990.0), methacryloxymethyltrimethoxysilane (IM6483.0), methacryloxypropyltrimethoxysilane (SIM6487.4), methacryloxypropyltris(vinyldimethylsiloxy)silane (SIM6487.8), tetraallylsilane (SIT7020.0), norbornenyltriethoxysilane (SIB0992.0), vinyltriethoxysilane (Geniosil GF 56) vinyltris(2-methoxyethoxy)silane (Geniosil GF 58), vinyltriacetoxysilane (Geniosil GF 62), (3-mehtacryloxypropyl)trimethoxysilane (Geniosil GF 31), (methacryloxymethyl)methyldimethoxysilane (Geniosil XL 32), (methacryloxymethyl)trimethoxysilane (Geniosil XL 33), (methacryloxymethyl)methyldiethoxysilane (Geniosil XL 34), (methacryloxymethyl)triethoxysilane (Geniosil XL 36), and the like supplied by ABCR GmbH & Co. KG and Wacker –Chemie GmbH. Typical examples of vinyl functionalized POSS compounds are: styrenylisobutyl-POSS (ST1506), styrylcyclohexyl-POSS (ST1509), styrylcyclopentyl-POSS (ST1510, styrylisobutyl-POSS (ST1515), allylcyclohexyl-POSS (OL1099), allylcyclopentyl-POSS (OL1100), allylisobutyl-POSS (OL1118), allyldimethylsilylcyclopentyl-POSS (OL1105), cyclohexenylethylcyclopentyl-POSS (OL1110), allylcyclohexyl-POSS (OL1099), allylcyclopentyl-POSS (OL1100), allylisobutyl-POSS (OL1118), allyldimethylsilylcyclopentyl-POSS (OL1105), cyclohexenylethylcyclopentyl-POSS (OL1110), allylisobutyl-POSS (OL1118), allyldimethylsilylcyclopentyl-POSS (OL1105), cyclohexenylethylcyclopentyl-POSS (OL1110), dimethylvinylcyclopentyl-POSS (OL1114), diphenylvinylcyclopentyl-POSS (OL1117), monovinylcyclohexyl-POSS (OL1122), monovinylcyclopentyl-POSS (OL1120), monovinylisobutyl-POSS (OL1123), phenylmethylvinylcyclopentyl-POSS (OL1125), tris(dimethylvinyl)cyclopentyl-POSS (OL1154),

tris(dimethylvinyl)cyclopentyl-POSS (OL1155), tris(dimethylvinyl)isobutyl-POSS (OL1119), trivinylsilylcyclopentyl-POSS (OL1157), methacrylfluoro(3)cyclo[pentyl-POSS (MA0720), methacrylfluoro(13)cyclopentyl-POSS (MA0730), methacryltrimethylsiloxycyclopentyl-POSS (MA0740), methacryltrimethylsiloxyisobutyl-POSS (MA0742), methacrylisobutyl-POSS (MA0702), methacrylisooctyl-POSS (MA0719), methacrylphenyl-POSS (MA0734), methacryldisilanolcyclohexyl-POSS (MA0715), methacryldisilanolcyclopentyl-POSS (MA0711), methacryldisilanolisobutyl-POSS (MA0713), methacryl-POSS cage mixture (MA0735), octamethacryldimethylsilyl-POSS (MA0745), tris(methacryl)cyclohexyl-POSS (MA0747), trismethacrylisobutyl-POSS (MA0750), acrylocyclehexyl-POSS (MA0699), acrylocyclopentyl-POSS (MA0700), acryloisobutyl-POSS (MA0701), methacrylcyclohexyl-POSS (MA0704), methacrylcyclopentyl-POSS (MA0705), methacrylethyl-POSS (MA0717), octacyclohexenyldimethylsilyl-POSS (OL1159), octavinyldimethylsilyl-POSS (OL1163), octavinyl-POSS (OL1160), vinyl-POSS cage mixture (OL1170) and tetra vinyl-T2 (OL1150) and the like supplied by Hybrid Plastics (USA).

Other ingredients

Small amounts of inhibitors such as hydroquinone can be used in order to prevent or limit degradation of the (meth)acrylate monomers during storage. Other substances that can prolong the stability of (meth)acrylate monomers and are known in prior art or in the literature may well be also included. Inhibitors may be added in an amount that does not reduce the rate of polymerization or the ultimate properties of an adhesive or other composition made therewith, typically about 10^2-10^4 ppm based on the weight of the polymerizable monomers.

Epoxy compounds can be included in the adhesive compositions of the invention in amounts from 0 to about 50%, preferably 0 to about 25% weight based on the total weight of the composition. The epoxy resin may be any thermosettable resin having an average of more than one (preferably, about two or more) epoxy groups per molecule. Epoxy resins are well known in the art and are described, for example, in the chapter entitled "Epoxy Resins" in the Second Edition of the Encyclopedia of Polymer Science and Engineering, Volume 6, pp. 322-382 (1986). Suitable epoxy resins include polyglycidyl ethers obtained by reacting polyhydric phenols such as bisphenol-A, bisphenol-F, bisphenol AD, catechol, or resorcinol, or polyhydric aliphatic alcohols such as glycerin, sorbitol, pentaerythritol, trimethylol propane and polyalkylene glycols with haloepoxides such as epichlorohydrin; glycidylether esters obtained by reacting hydroxycarboxylic acids such as p-hydroxybenzoic acid or beta-hydroxy naphthoic acid with epichlorohydrin or the like; polyglycidyl esters obtained by reacting polycarboxylic acids such as phthalic acid, tetrahydrophthalic acid or terephthalic acid with epichlorohydrin or the like; epoxidated phenolic-novolac resins (sometimes also referred to as polyglycidyl ethers of phenolic novolac compounds); epoxidated polyolefins; glycidylated aminoalcohol compounds and aminophenol compounds, hydantoin diepoxides and urethane-modified epoxy resins.

An epoxy-terminated amine-epoxy adduct, that is to say an adduct between one or more molecules containing at least two epoxy rings and one or more compounds containing at least one amine groups such that there is a stoichiometric excess of the epoxy rings. Carboxylic acid anhydrides, carboxylic acids, phenolic novolac resins, thiols (mercaptans), water, metal salts and the like may also be utilized as additional reactants in the preparation of the amine-epoxy adduct or to further modify the adduct once the amine and epoxy have been reacted.

Specific examples of suitable commercially available epoxy resins are those sold under the trade mark ARALDITE such as the MY-series (e.g. MY-0500, MY-0510, MY-0501, MY-720, MY-740, MY-750, MY-757, MY-790, MY-791, etc.), the GY-series (e.g. GY-240, GY-250, GY-260, GY-261, GY-282, etc.) (HUNTSMAN (previously VANTICO A.G., Switzerland), DER-324, DER-332, DEN-431, DER-732 (DOW Chemical Co., USA), EPON 813, EPON 8021, EPON 8091, EPON 825, EPON 828, Eponex 1510, Eponex 1511 (SHELL Chemical Co. USA), PEP 6180, PEP 6769, PEP 6760 (Pacific Epoxy Polymers Inc. USA), NPEF-165 (Nan Ya Plastic Corporation, Republic of China), Ricopoxy 30, Ricotuff 1000-A, Ricotuff-1100-A, Ricotuff-1110-A (Ricon Resins Inc., USA), Setalux AA-8502, Setalux 8503 (AKZO Nobel, Netherlands), to mention just a few.

Another useful adjuvant is a cross-linking agent. Cross-linking agents can be used to enhance the solvent resistance of the adhesive bond or polymer composition. The cross-linking agent can increase the use temperature and the solvent resistance of the cured polymer or adhesive. Typically

employed in an amount of 0.1 to 20% w/w based on the total weight of the compositions, useful cross-linkers include the various diacrylates, referred to above as possible acrylic modifying monomers, and compounds with acrylate and isocyanate functionality as well as other materials. Particular examples of suitable cross-linking agents include ethylene glycol, dimethacrylate, ethylene glycol diacrylates, triethylene glycol dimethacrylate, diethylene glycol dimethacrylate, diethylene glycol bismethacryloxy carbonate, polyethylene glycol diacrylates, tetraethylene glycol dimethacrylate, diglycerol diacrylates, diethylene glycol dimethacrylate, pentaerythritol triacrylate, trimethacrylate tris(2-methyl-1-aziridinepropionate, trimethylolpropane trimethacrylate, acrylate tipped polyurethane containing prepolymers, polyether diacrylates and dimethacrylates.

The compositions of the present invention optionally include a phosphorous-containing compound having one or more olefinic groups and at least one P-OH group. This class of compounds is in essence described in p. 23-24, WO 03/040151.

The compositions of the present investigation may also contain metal salts as those described in detail in WO 03/057791. These metal salts can modify the curing kinetics of a polymerizable composition and are known in the art as "metal salt modifiers".

The compositions may optionally contain a non-organoborane-based free radical initiator (aerobic initiator), which are well known in the art. A non-organoborane free radical initiator can readily be contained in the polymerizable monomer part of a two-part polymerizable composition. Preferred non-organoborane free radical initiators are those, which do not readily react with monomer under shelf-aging conditions, or can be inhibited suitably to provide desired shelf stability of up to several months, if needed. Illustrative examples of suitable non-organoborane-based free radical initiators include organic peroxides and organic hydroperoxy initiators, particularly those organic hydroperoxides having the formula R'OOH where in R' is a hydrocarbon radical containing up to about 20 carbon atoms, preferably an alkyl, aryl or arylalkyl radical of 1 up to 14 carbon atoms. Specific examples of such hydroperoxides are cumene hydroperoxide, tertiary butyl hydroperoxide, methyl ethyl ketone peroxide and peroxides formed by the oxygenation of various hydrocarbons such as methylbutene, cetane, and cyclohexane and various ketones and ethers. Other examples of useful initiators include hydroperoxides such as p-menthane hydroperoxide, 2,5-dimethylhexane, 2,5-dihydroxyperoxide and the like and also silyl-type peroxides. Some (not all) types of compounds that can be useful as aerobic initiators are also described in essence in US 4,043,982. Additionally, more than one non-organoborane-based free radical initiators may be employed, such as a mixture of hydroperoxides with peresters, such as t-butyl perbenzoate or *t*-butyl-peroxymaleate can be advantageously used. Cumene hydroperoxide is especially preferred.

The compositions of the invention may contain a reactive or non-reactive diluent to balance the volume of the two parts of the composition so as to achieve a commercially acceptable volumetric ratio of the two components. Preferably the diluent is a reactive diluent. Preferred reactive diluents are isocyanate reactive compounds as in essence described in WO 03/038006, 1,4-dioxo-2-butene functional materials as in essence described in WO 00/56779, aziridine functional materials as in essence described in WO 98/17694 WO 99/64528, WO 99/64475, various types of waxes e.g. petroleum [paraffin (crystalline) wax, microcrystalline wax and petroleum wax], vegetable (typical examples: carnauba wax, Japan wax, ouricury wax, rice-bran wax, jojoba wax, castor wax, bayberry wax, soy bean wax, etc.) insect and animal (typical examples: beeswax, spermaceti wax, Chinese wax, wool wax, shellac wax, etc.), mineral (typical examples: montan wax, peat wax, ozokerite wax, ceresin wax, etc.), synthetic waxes (typical examples: polyethylene waxes, a-olefin waxes, carbowaxes, halowaxes, etc.), etc., as in essence described in WO 03/035703, unsaturated hydrocarbons such as 2,6-dimethyl-2,4,6-octatriene and the like, and mostly desirable any liquid complex of those described by the general formula II. Another class of desirable diluents include those selected from certain ethers, epoxies, and hydrocarbons and more specifically poly(tetrahydrofurane), 2-haloalkyl phenyl ethers such as 2-bromoethyl phenyl ether, 2-chloro ethyl phenyl ethyl, glycidoxy alkyltrialkoxy silanes such as 3-glycidoxypropyltrimehoxysilane, certain glycidyl ethers such as glycidyl heptyl ether, glycidyl undecyl ether, glycidyl ether, glycidyl heptyl ether, propanediol diglycidyl ether, butenediol glycidyl ether, cyclohexane dimethanol diglycidyl ether, 2-ethyl hexyl glycidylether, 1-benzyl-2,3-isopropylidene-S/N-glycerol, and the like. Triglyme and tetraglyme are particularly desirable.

The compositions may further comprise a variety of optional additives. The various optional additives are employed in an amount that does not significantly adversely affect the polymerization

process of the desired properties of compositions made therewith. The quantity of thixotropic agent(s) is desirably adjusted so as to provide a dough, which does not exhibit any tendency to flow at room temperature. One particularly useful additive is a thickener such as medium to high (10.000 to 1.000.000 a.u.) molecular weight poly(methyl methacrylate) which may be incorporated in an amount of 0.1-60% w/w, preferably in an amount of 0.2-20% w/w, and most preferably of 0.4-10% w/w, based on the total weight of the composition. Thickeners may be employed to increase the viscosity of the composition to facilitate application of the composition. Preferable materials of this class are poly(methyl methacrylate) homo- and co-polymers under the trademark ELVACITE commercially available from Lucite International and also styrene/methyl methacrylate co-polymers and polybisphenol-A maleate or propoxylated bisphenol-A fumarate polyester (trademark ATLAC). It is also possible to add inert filling materials such as finely divided silica, fumed silica (treated or untreated) (e.g. tradename AEROSIL), montmorillonite, clay, bentonite and the like. The use of microionized silica would result in a paste-like thixotropic composition. Polymeric thickeners or other thickeners such as silicas may suitably be present –in a two-component composition- as a thickener for the diluent in the hardener's part.

Another particularly useful additive is an elastomeric material. The materials may improve the fracture toughness of compositions made therewith which can be beneficial when, for example, bonding stiff, high yield strength materials such as metals substrates that do not mechanically absorb energy as easily as other materials, such as flexible polymeric substrates. Such additives can be incorporated in an amount of 5-50% w/w, based on the total weight of the composition. Preferably these elastomers of rubber polymers are those based on polyisoprenes, polybutadienes (homo- and co-polymers), polyolefines, polyurethane, polyesters, etc. Typical examples of elastomeric materials include homopolymers such as polybutadiene, polyisoprene and polyisobutylene; diene type copolymers such as butadiene/styrene copolymer, butadiene/acrylonitrile copolymer, butadiene/methyl methacrylate copolymer and butadiene/alkyl acrylate copolymer; ethylene/vinyl acetate copolymers; ethylene/alkyl acrylate copolymers (1-8) carbons in the alkyl group), rubbery polyalkyl acrylates or copolymers thereof; polyurethane; chlorinated polyethylenes; and EPDM (ethylene/propylene/diene terpolymers). The elastomers of these structures may contain a functional group at one or both ends or within a particular segment or repeating unit of the copolymer. Among the suitable functional groups are vinyl, epoxy, carboxyalkyl and mercapto groups. Other functional groups may be employed as deemed useful and upon proper experimentation. Useful elastomeric modifiers include chlorinated or chlorosulphonated polyethylenes such as HYPALON 30 and block copolymers of styrene and conjugated dienes (trademarks: VECTOR, KRATON, STEREON). Also useful and even more preferred are certain graft copolymer resins such as particles that comprise rubber or rubber-like cores or networks that are surrounded by relatively hard shells, these materials often being referred to as "core-shell" polymers. Most preferred are the acrylonitrile/butadiene/styrene and methyl methacrylate/butadiene/styrene graft copolymers. In addition, to improve the fracture toughness of the composition, core shell polymers can also impart enhanced spreading and flow properties to the uncured composition. These enhanced properties may be manifested by a reduced tendency for the composition to leave an undesirable "string" upon dispensing from a syringe-type applicator, or sag or slump after having been applied to a vertical surface. Use of more than 10% w/w of a core shell polymer additive is desirable for achieving improved sag-slump resistance. Generally, the amount of toughening polymer used is that amount which gives the desired toughness to the polymer or to the adhesive prepared.

The compositions of the invention can contain a heat management material. Any material, which functions to dissipate heat during polymerization, may be used. Examples of useful heat management materials include volatile liquids, which evaporate during the reaction as a result of absorbing heat-generated heat, and materials, which react via an endothermic reaction under conditions of the reaction. Materials useful as heat sinks are materials with high heat capacities. Examples of materials with high heat capacities include ceramic particles, glass beads, fluoropolymer powders (e.g. TEFLON powders) and hollow spheres. In the case of adhesives the role of glass beads and hollow spheres can be also that of bond spacer controllers. Useful liquid materials include, chlorinated alkanes, dialkyl ethers, alkanes, methylene chloride and low boiling point petroleum ethers. More preferred solvents include methylene chloride, diethyl ether, pentane and hexane. The amount of heat management material used is dependent on the target reaction temperature and the heat capacity of the heat management material. The heat of reaction can also be impacted by slowing down the rate of mixing thereby allowing for slower heat generation. Preferably the average temperature of the adhesive (when the curing of the later is not triggered by

heating, or by the application of actinic radiation or by electromagnetic radiation or by magnetic radiation, electrical current, ultrasounds, ultraviolet radiation combinations thereof or any other means that result to the aforementioned specie of radiation or heat) over its working time is managed to a target of 70°C or less, preferably 60°C or less and most preferably 50°C or less. The heat management material can be placed on either the resin side (polymerizable mixture) of the formulation or on the hardener side. The selection of the heat management material and its amount are driven by the amount of heat that needs to be dissipated during the polymerization. If the heat generated during the reaction is too high for too long of a period of time, the adhesion of the polymerized composition to a substrate may be negatively impacted.

The composition may also contain known catalysts for the reaction of an isocyanate reactive compound with an isocyanate-containing compound or for the reaction of an epoxy reactive material with an epoxy-containing compound.

The compositions may also include one or more of the following: fillers (e.g. alumina, glass powder, ceramic powder and metal powder) that may also contribute to the rheological control of the composition different to those mentioned already in the paragraph associated to thixotropic agents; reinforcement fibres, e.g. glass-, carbon-, basalt wollastonite, ceramic, aramid fibres and mixtures thereof; silicone rubbers, silicone core-shell particles; reinforcing agents and/or pigments e.g. metal oxides, metal hydrates, metal hydroxides, metal aluminates, metal carbonates/sulphates, starches, talcs, kaolins, molecular sieves, organic pigments, etc.); solvents (they should be selected to have boiling points below the thermal dissociation temperature of the organosilicon organoborane complex); other flow modifiers;other calcium carbonate (including coated and/or precipitated calcium carbonate, which may also act as a thixotropic or rheological control agent, especially when it is in the form of fine particles), alumina, clays, nanoclays (e.g. natural montmorillonites, etc.), or nano-organoclays (e.g. intercalated montmorillonites, etc.) or modified sand, metals (e.g., aluminum powder), microspheres (glass microspheres, thermoplastic resin, ceramic and carbon microspheres, which may be solid or hollow, expanded or expandable), and any of the other organic or inorganic fillers known in the art; additives commonly used in adhesives, sealants, paints and coatings, casting resins, cables, in shapable moulding materials and in finished mouldings or in composite materials; plasticizers, ;adhesion promoters (also known as wetting or coupling agents; e.g., silanes, titanates, zirconates), colorants (e.g., dyes and pigments such as carbon black), stabilizers (e.g., antioxidants, UV stabilizers), and the like; coloring agents (pigments and dyes); antifoaming agents; leveling agents; flame retardants; antioxidants; etc.

<u>Methods of application and bonded articles</u>

The novel two-part polymerisable compositions of the present invention can be prepared in a known manner by, for example, premixing individual components and then mixing these premixes, or by mixing all of the components using customary devices, such as stirred vessels, often at slightly elevated temperature. The physical form of the composition and its constituent parts will depend upon the intended application, and may for example be a powder, a paste, or a liquid. The formulation of products as a liquid is often preferred for commercial applications.

When the compositions of this invention are formulated as a two-part product, the two parts may be mixed for curing in any suitable ratio; they may for example be presented in packs containing convenient whole number mix ratio of 1:50 or less, for example 1:10, 1:4, 1:3, 1:2 or 1:1, such that they can easily be used with two-part dispensers. For a two-part adhesive such as those of the invention to be most easily used in commercial and industrial environments, the ratio at which the two parts are combined should be a convenient whole number. This facilitates application of the adhesive with conventional, commercially available dispensers (e.g. under the trademark "MixPac®"). Such dispensers are sometimes described as dual syringe-type applicators. Detailed description of such dispensers and their mode of application can be found in WO00/56779, U.S. 4,538,920, U.S. 5,082,147. For best commercial and industrial utility and for ease of use with currently available dispensing equipment, the two parts of the adhesive should be capable of being combined in a common, whole number mixing ratio such as 1:50 or less, more preferably 1:10, 1:4, 1:3, 1:2 or 1:1.

The polymerizable composition can be easily applied and cured at ambient temperature. Typically, it is applied to one or both substrates and then the substrates are joined together with pressure to force excess compositions out of the bond line. In general, the bonds should be made shortly after the composition has been applied, preferably within about 3 h and more preferable in less than 2 h.

The typical bond line thickness is about 30-1000 microns, preferably 50-500 and most preferably 80-350. The bonding can be easily carried out at room temperature. The bonds preferably cure to a reasonable handling strength (0.4 MPa) within 3 hours and most preferably less than 2. Full strength is reached in about 24-48 hours and more preferably in about 10-18 or most preferably in less than 10; post-curing with heat (typically about 35-180°C, preferably about 40-120°C and most preferably 50-90°C) may be used if desired. Even more rapid strength build-up is facilitated by the inclusion of crosslinking agents or cyclic anhydride-functional or vinyl unsaturated anhydride-functional reactive compounds in the polymerizing mixture.

The following data and examples illustrate the invention:

Raw Materials

The raw materials and supplier details are presented in Table 1.

Table 1

Raw material	Supplier	Description	Data
Triethylborane (TEB) in tetrahydrofuran (THF)	CALLERY	Solution of TEB in THF	14.5 % w/w TEB in THF
Sartomer R-203 (Tetrahydrofurfuryl methacrylate) (THFMA)	SARTOMER	Methacrylate	MW= 170.2 a.u.
2-Ethylhexyl methacrylate (EHMA)	ALDRICH	Methacrylate	MW= 198.31 a.u.
Trimethylolpropane trimethacrylate (TMPTA)	ALDRICH	Methacrylate	MW= 338.4 a.u.
BLENDEX 360	GE Specialty Chemicals	ABS rubber	50% Butadiene, particle size= 250 microns
ELVACITE 2010	LUCITE Intl.	Poly(methyl methacrylate)	MW= 80.000 a.u.
MY-0510	HUNTSMAN	Epoxy resin	Epoxy equivalent weight= 101, functionality=3
Fillite 160W	TRELLEBORG FILLITE Ltd.	Ceramic cenospheres	Particle size (% passing): 100% 180 microns, 28% 100 microns
AEROSIL 200	DEGUSSA	Hydrophilic fumed silica	BET surface area= 200+/- 25 m^2/g, average primary particle size= 12 nm
Trimethylolpropane tris(2-methyl-1-aziridinepropionate)	ALDRICH	Aziridine	MW= 467.61 a.u.
KF-857	SHIN-ETSU	Organoamino functinalized silicone	Amine equivalent weight= 800 a.u. (amino functionality: 3)
X22-161AS	SHIN-ETSU	Organoamino functinalized silicone	Amine equivalent weight= 415 a.u. (amino functionality: 2)
KBM-603	SHIN-ETSU	3-(2-Aminoethylamino)propyltrimethoxy silane	MW= 222.4 a.u.
KBE-903	SHIN-ETSU	(3-Aminopropyl)triethoxy silane	MW= 221.4 a.u.
KBM-903	SHIN-ETSU	(3-Aminopropyl)trimethoxy silane	MW= 179.1 a.u.
SLM-88705	WACKER	(Aminomethyl)trimethoxy silane	MW= 165.3 a.u.
AM0270	HYBRID PLASTICS	Aminopropylisooctyl-POSS	MW= 1267 a.u.
Glutaric acid (GA)	ALDRICH		MW= 132.1 a.u
Methacrylic acid (MA)	ALDRICH		MW= 86.1 a.u.
Succinic anhydride (SA)	ALDRICH		MW= 100.1 a.u.
Methacrylic anhydride (MAN)	ALDRICH		MW= 154.2 a.u.
Mono-2-(methacryloyloxy)ethyl maleate (MEM)	ALDRICH		MW= 228.2 a.u.
Mono-2-(methacryloyloxy)ethyl succinate (MES)	ALDRICH		MW= 230.2 a.u.

Pyrophoricity of organosilicon organoborane complexes

The pyrophoricity of organosilicon organoborane complexes was tested according to the method described in U.S. 5,690,780.

Thermal disassociation of organosilicon organoborane complexes

The thermal disassociation of organosilicon organoborane complexes was assessed by Differential Scanning Calorimetry (DSC). DSC measurements from –40°C to 280°C, were carried out on a Mettler 820, in air atmosphere at a heating rate of 20°C/min. The onset temperature of the exotherm due to the organosilicon organoborane complex's disassociation was recorded (disassociation temperature).

Adhesive test methods

Polypropylene, polypropylene copolymer, polyvinyl chloride, polytetrafluoroethylene, polymethylmethacrylate substrates and aluminium were degreased by wiping with tissue paper soaked in acetone. Polycarbonate, low and high density polyethylene as well as ABS substrates were degreased with isopropanol. No surface abrasion, priming, or other surface pre-treatment was applied in the case of plastic substrates. All the plastic substrates were purchased from Engineering and Design Plastics Ltd. (Cambridge, U.K., www.edplastics.co.uk). Steel substrates were sandblasted. The adhesive composition was dispensed onto one face of each substrate pair. The two substrates were mated (see Table 2 for bond area) and held to each other with two bulldog clamps. Small amounts of adhesive squeezed out of the overlapped area were allowed to remain. The dimensions and bonded areas of the test coupons are shown in Table 2.

The bonded joints were left to cure for 48h at 25°C (unless otherwise stated). The clamps were then removed and the bonded joints were tested for tensile shear strength (TSS) on a tensile tester (Instron 4467) at crosshead speed of 2.54 mm/min according to ISO 4587. The TSS values were recorded in megapascals (MPa) and the failure mode is reported as:

AF (adhesive failure): delamination between adhesive and substrate.
CF (cohesive failure): failure within the adhesive layer.
SF (substrate failure): bonded substrate breaks.
SN (substrate necking: bonded substrate yields (plastic deformation).

Table 2

Substrates of the overlap bond pair	Width (mm)	Length (mm)	Thickness (mm)	Bond area (widthx125mm) (mm^2)
Polytetrafluoroethylene (PTFE-PTFE)	20	85	4	250.0
Polytetrafluoroethylene (PTFE6-PTFE6)	20	85	6	250.0
Polypropylene (PP-PP)	25	85	3	312.5
Polypropylene copolymer (CPP-CPP)	25	85	3	312.5
Low density polyethylene (LDPE-LDPE)	25	85	3	312.5
High density polyethylene (HDPE-HDPE)	25	85	3	312.5
Polyvinyl chloride (PVC-PVC)	25	85	3	312.5
Poly(methyl methacrylate) (PMMA-PMMA)	25	75	3	312.5
Poly(Acrylonitrile-Butadiene-Styrene) (ABS-ABS)	25	85	3	312.5
Polycarbonate (PC-PC)	25	85	3	312.5
Aluminium (AL-AL)	25	115	1	312.5
Steel (STL-STL)	25	115	1	312.5
Polypropylene & Steel (PP-STL)	25	85/115	3/1	312.5

The strength build-up (tensile shear stress *vs.* curing time) of a competitor's product (COPR) on a polypropylene-polypropylene joint was also evaluated and compared to the strength of an adhesive formulation prepared herein. A series of joints has been prepared by applying the COPR to both substrates via a dual-syringe-type applicator (10:1 v/v). The joints prepared as mentioned here before, left to cure for 1, 2, 4, 6 and 24 h at 23°C.

Examples

Example 1
Synthesis of organoborane complexes

The complexation reactions between triethylborane (TEB) and the complexing agents were carried out in N_2 atmosphere. A 50-mL conical flask was charged with the complexing agent (or a solution of the complexing agent in a volatile solvent preferably THF) and it was placed into an ice-bath and on an analytical scale. The required amount of TEB (14.5% w/w, tetrahydrofurane (THF) solution) was transferred via a syringe into the conical flask. Upon completion of the addition of TEB, the reaction mixture (along with the ice-bath) was removed from the analytical scale and was stirred for 4-6h. The flask was then removed from the inert atmosphere and left at ambient temperature in air for 3 to 5 days for the THF to evaporate. The evaporation process was tracked via weight loss measurements over time. The evaporation process was considered complete when no further weight loss was recorded, which takes into account weight loss due to any hydrolysis products. Table 3 presents the newly synthesized complexes, which are storage, stable at ambient temperature and none of them is pyrophoric.

Table 3

Organoborane complex (Part B)	Complexing Agent	Mol Ratio (TEB/complexing agent)	Physical State
C1	KF-857	1:1	Transparent liquid
C2	KF-857	2:1	Transparent liquid
C3	KF-857	3:1	Transparent liquid
C4	KF-857	7:1	Transparent liquid
C5	X22-161AS	2:1	Transparent liquid
C6	X22-161AS	3:1	Transparent liquid
C7	AM0270	1:1	Yellow liquid
C8	AM0270	3:1	Yellow liquid
C9	KBM-603	1:1	Transparent liquid
C10	KBM-603	2:1	Transparent liquid
C11	KBM-903	1:1	Transparent liquid
C12	KBE-903	1:1	Transparent liquid
C13	SLM-88705	1:1	White solid

All the above complexes showed different disassociation temperatures all higher than 25°, for example the disassociation temperatures of C1 and C3 were 65 and 45°C respectively.

Example 2

In some cases the aforementioned complexes were combined with aziridine or with each other. Table 4 depicts these combinations.

Table 4

Mixture of Organoborane Complex (Part B)	Organoborane complex A	Organoborane complex B	Diluent	Weight Ratio (Organoborane complex A/ Organoborane Complex B)	Weight Ratio (Organoborane complex A/ Diluent)
C14	C9	——	aziridine	——	2.3
C15	C12	C2	——	1.5	——
C16	C12	C3	——	1.5	——
C17	C12	C7	——	1.5	——
C18	C9	C1	——	2.7	——
C19	C9	C7	——	2.7	——
C20	C10	——	aziridine	——	1.0
C21	C12	C5	——	1.5	——
C22	C12	C6	——	1.5	——
C23	C12	——	aziridine	——	2.3

Example 3

General preparation procedure for Part A of the adhesives

A mixture of methacrylates, the decomplexer (or a solution of the decomplexer in THFMA in cases where the decomplexer is a solid), BLENDEX-360 and ELVACITE-2010 were sheared in a high-shear mixer at approx. 3000 rpm for 1 h. FILLITE-160W was then added to the slurry and mixing was continued for another 10 min at 500 rpm.

In some cases (A1-A10, Table 5) after 1 h of mixing the methacrylates, decomplexer, BLENDEX-360 and ELVACITE-2010, an addition of AEROSIL 200 to the mixture was made, and mixing continued at 3000 rpm for another 10 min. At the end FILLITE-160W was added to the slurry and mixing continued for another 10 min.

In one case (A11, Table 5), epoxy resin MY-0510 was added to the mixture of methacrylates, decomplexer BLENDEX-360 and ELVACITE-2010. After 1 h of mixing, AEROSIL 200 was added and mixing at 3000 rpm continued for another 10 min. At the end FILLITE-160W was added to the slurry and mixing continued for another 10 min.

In one case (A39, Table 5), no decomplexer was added to the mixture of methacrylates, BLENDEX-360 and ELVACITE-2010. After 1 h of mixing, FILLITE-160W was added to the slurry and mixing continued for another 10 min.

A series of different compositions of Part A of the adhesives is depicted in Table 5.

Table 5

		Methacrylates			Decomplexer						Epoxy Resin	ABS-Rubber	Acrylic Resin	Thixotrope	Ceramic Cenospheres
Example	Adhesive (part A)	THFMA (% w/w)	EHMA (% w/w)	TMPTA (% w/w)	MEM % w/w)	MES (% w/w)	MAN (% w/w)	MAI (% w/w)	SAI (% w/w)	GA (% w/w)	MY-0510 (% w/w)	BLENDEX 360 (% w/w)	ELVACITE 2010 (% w/w)	AEROSIL 200 (% w/w)	FILLITE 160W (% w/w)
1	A1	51.66	18.96		13.06							10.30		0.86	5.16
2	A2	54.30	19.93		8.59							10.86		0.90	5.42
3	A3	55.31	20.30		6.89							11.06		0.92	5.52
4	A4	53.79	19.74		9.44							10.76		0.90	5.37
5	A5	55.19	20.26		7.08							11.04		0.92	5.51
6	A6	57.97	21.28		2.40							11.59		0.87	5.79
7	A7	57.06	20.94		3.94							11.41		0.95	5.70
8	A8	56.61	20.78		4.70							11.32		0.94	5.65
9	A9	50.43	18.51		15.10							10.09		0.84	5.03
10	A10	57.57	21.13					3.08				11.51		0.96	5.75
11	A11	49.18	18.05		8.63						8.57	9.84		0.82	4.91
12	A12	51.87	17.29		3.94							17.30	4.80		4.80
13	A13	51.66	17.22		4.33							17.23	4.78		4.78
14	A14	50.67	16.89		6.16							16.90	4.69		4.69
15	A15	49.24	16.41		8.81							16.42	4.56		4.56
16	A16	53.10	17.70					1.67				17.69	4.92		4.92
17	A17	52.27	17.42			3.20						17.43	4.84		4.84
18	A18	52.99	17.66							1.86		17.67	4.91		4.91
19	A19	53.23	17.74						1.42			17.75	4.93		4.93
20	A20	52.61	17.54		2.56							20.47	1.95		4.87
21	A21	50.11	16.70		7.21							19.48	1.86		4.64
22	A22	50.09	16.70		7.24							19.47	1.86		4.64
23	A23	50.34	16.78		6.79							19.57	1.86		4.66
24	A24	50.12	16.71		7.18							19.49	1.86		4.64
25	A25	51.46	17.15		4.70							20.02	1.91		4.76
26	A26	50.97	16.99		5.62							19.81	1.89		4.72
27	A27	51.10	17.03		5.37							19.88	1.89		4.73
28	A28	51.14	17.05		5.30							19.89	1.89		4.73
29	A29	50.69	16.90		6.13							19.71	1.88		4.69
30	A30	50.51	16.84		6.47							19.63	1.87		4.68
31	A31	51.11	17.04		5.35							19.88	1.89		4.73
32	A32	48.15	16.05		10.83							18.73	1.78		4.46
33	A33	50.38	16.79		6.70							19.59	1.87		4.67
34	A34	49.65	16.55		8.05							19.31	1.84		4.60
35	A35	51.02	17.01		5.51							17.01	4.72		4.73
36	A36	55.10	20.22		7.24							11.02		0.92	5.50
37	A37	49.90	16.63		7.59							19.41	1.85		4.62
38	A38	51.17	17.06		5.24							17.06	4.74		4.73
39	A39	54.00	18.00									18.00	5.00		5.00
40	A40	51.50	17.17		4.63							17.17	4.77		4.76
41	A41	50.18	16.73		7.07							16.73	4.65		4.64
42	A42	49.87	16.62		7.64							16.62	4.62		4.63
43	A43	50.79	16.93		5.94							19.75	1.88		4.71
44	A44	52.59	17.53		2.60							20.45	1.95		4.88
45	A45	49.59	16.53		8.17							19.28	1.84		4.59
46	A46	52.10	17.37		3.52							20.36	1.93		4.72
47	A47	51.56	12.41	4.77	4.52							18.14	4.77		3.83
48	A48	50.33	16.78		6.80							19.57	1.86		4.66

Example 4

A series of two-component acrylic adhesives was prepared (see Table 6, AF series), using as Part A compositions A1-A48 (Example 3, Table 5) and as initiator (Part B) the organoborane complexes C1-C22 (Examples 1 & 2, Tables 3 & 4). The components were mixed immediately prior to bonding the substrates. Overlap shear specimens were prepared and tested according to the adhesion test method described here before. Table 6 gives details of the adhesive compositions, the ratios of Part A and Part B, and the tensile shear strength results and failure mode of bonded joints of various substrates.

In one case (No.43, Table 6), the bonded joint was left to cure for 24 h at 23°C.

In one case (No.63, Table 6), the bonded joint was left to cure for 1 h at 80°C. After cooling the joint down to ambient temperature, the joint was tested for tensile shear strength (TSS) similarly as all the other joints prepared herein.

Example 5

Table 7, presents data regarding typical strength build-up (tensile shear strength *vs.* curing time @ 23°C for PP-joints) of the adhesive formulation AF43 prepared in Example 4 (Table 6) and for a competitor's product (CORP). The curing time for both adhesives was: 0.5, 1, 2, 4, 6 and 24h). AF43 develops handling strength (0.4 MPa) in about 1 h and maximum strength (substrate failure) in about 7-10 h. It becomes evident that this particular formulation outperforms the competitor's product (COPR) as it develops strength faster (handling strength achieved after only 1h whilst the corresponding figure for the COPR was 2h).

Table 7

	AF43			CORP		
Curing time (h)	TSS (MPa)	% Max. strength*	Failure mode	TSS (MPa)	% Max. strength*	Failure mode
0.5	0.29	4.79	AF	0.12	2.02	AF
1	0.45	7.44	AF	0.23	3.87	AF
2	1.65	27.27	CF	0.40	6.73	AF
4	3.68	60.83	CF	1.70	28.61	CF
6	4.59	75.87	CF	3.94	66.31	CF
24	6.05	100.00	SF	5.94	100.00	SF

**the % max. strength for each of the adhesives of the.Table is equal to: TSS recorded upon certain curing time multiplied by 16.53 in the case of AF43 or by 16.83 in the case of CORP).*

No	Adhesive Formulation	Part A	Part B	Part A (% w/w)	Part B (% w/w)	Adhesion Strength		
						Joint (substrate-substrate)	TSS (MPa)	Failure mode
1	AF1	A1	C3	66.1	33.9	PP-PP	3.32	CF
2	AF2	A2	C3	74.7	25.3	PP-PP	3.67	CF
3	AF3	A3	C3	78.7	21.3	PP-PP	3.31	CF
4	AF4	A11	C3	74.7	25.3	PP-PP	3.78	CF
5	AF5	A4	C3	72.9	27.1	PP-PP	3.78	CF
6	AF6	A5	C3	78.2	21.8	PP-PP	3.17	CF
7	AF7	A6	C10	97.2	2.8	PP-PP	4.12	CF
8	AF8	A7	C10	95.4	4.6	PP-PP	5.01	CF
9	AF9	A8	C10	94.6	5.4	PP-PP	4.91	CF
10	AF10	A9	C3	73.7	26.3	PP-PP	3.03	CF
11	AF11	A10	C3	73.6	26.4	PP-PP	3.34	CF
12	AF12	A12	C20	95.6	4.4	PP-PP	6.56	SF
13	AF13	A12	C12	95.4	4.6	PP-PP	5.42	SF
14	AF14	A13	C9	94.6	5.4	PP-PP	3.37	CF
15	AF15	A13	C10	94.6	5.4	PP-PP	6.76	SF
16	AF16	A13	C12	94.6	5.4	PP-PP	6.94	SF
17	AF17	A14	C14	94.0	6.0	PP-PP	3.09	CF
18	AF18	A14	C23	94.0	6.0	PP-PP	6.56	SF
19	AF19	A16	C12	94.4	5.6	PP-PP	4.54	CF
20	AF20	A17	C12	94.5	5.5	PP-PP	4.77	CF
21	AF21	A18	C12	94.4	5.6	PP-PP	6.36	SF
22	AF22	A19	C12	94.4	5.6	PP-PP	6.69	SF
23	AF23	A28	C17	90.9	9.1	PP-PP	4.05	CF
24	AF24	A27	C15	90.9	9.1	PP-PP	4.63	CF
25	AF25	A26	C16	90.9	9.1	PP-PP	5.64	SF
26	AF26	A29	C12	93.0	7.0	PP-PP	6.24	SF
27	AF27	A30	C9	91.8	8.2	PP-PP	3.47	CF
28	AF28	A31	C10	95.0	5.0	PP-PP	4.68	CF
29	AF29	A25	C12	94.6	5.4	PP-PP	5.27	SF
30	AF30	A33	C3	93.9	6.9	PP-PP	3.27	CF
31	AF31	A34	C18	90.8	9.2	PP-PP	3.21	CF
32	AF32	A14	C19	90.6	9.4	PP-PP	3.48	CF
33	AF33	A36	C4	87.8	12.2	PP-PP	2.54	CF
34	AF34	A24	C13	93.5	6.5	PP-PP	3.03	CF
35	AF35	A47	C11	94.6	5.4	PP-PP	1.36	CF
36	AF36	A38	C11	93.8	6.2	PP-PP	4.89	CF
37	AF37	A43	C11	93.0	7.0	PP-PP	3.74	CF
38	AF38	A44	C5	94.5	5.5	PP-PP	6.08	SF
39	AF39	A45	C5	84.5	15.5	PP-PP	3.80	CF
40	AF40	A46	C6	94.5	5.5	PP-PP	5.08	SF
41	AF41	A48	C6	89.9	10.1	PP-PP	2.86	CF
42	AF42	A41	C21	91.5	8.5	PP-PP	4.52	CF
43	AF43	A35	C12	94.6	5.4	PP-PP	6.05	SF
44	AF44	A42	C22	91.5	8.5	PP-PP	5.13	SF
45	AF45	A20	C8	85.1	14.9	CPP-CPP	3.44	CF
46	AF46	A21	C12	93.1	6.9	CPP-CPP	2.63	CF
47	AF47	A22	C9	91.9	8.1	CPP-CPP	4.53	SN
48	AF48	A23	C10	94.7	5.3	CPP-CPP	4.93	SN
49	AF49	A24	C13	93.5	6.5	CPP-CPP	2.28	CF
50	AF50	A25	C12	94.8	5.4	CPP-CPP	4.53	SN
51	AF51	A15	C3	74.3	25.7	CPP-CPP	2.48	CF
52	AF43	A35	C12	94.6	5.4	PC-PC	4.30	SF
53	AF43	A35	C12	94.6	5.4	PTFE-PTFE	3.90	CF
54	AF52	A40	C12	95.4	4.6	PTFE6-PTFE6	5.18	CF
55	AF53	A32	C10	94.9	5.1	ABS-ABS	4.36	SF
56	AF53	A32	C10	94.9	5.1	PVC-PVC	4.03	SF
57	AF54	A37	C9	91.5	8.5	PMMA-PMMA	3.81	SF
58	AF43	A35	C12	94.6	5.4	LDPE-LDPE	2.04	SN
59	AF43	A35	C12	94.6	5.4	HDPE-HDPE	5.02	SN
60	AF43	A35	C12	94.6	5.4	AL-AL	12.11	CF
61	AF43	A35	C12	94.6	5.4	STL-STL	13.62	CF
62	AF43	A35	C12	94.6	5.4	STL-PP	8.01	SF
63	AF55	A39	C12	94.4	5.6	PP-PP	3.32	AF

Table 6

Claims:

1. A complex of a compound of the general formula

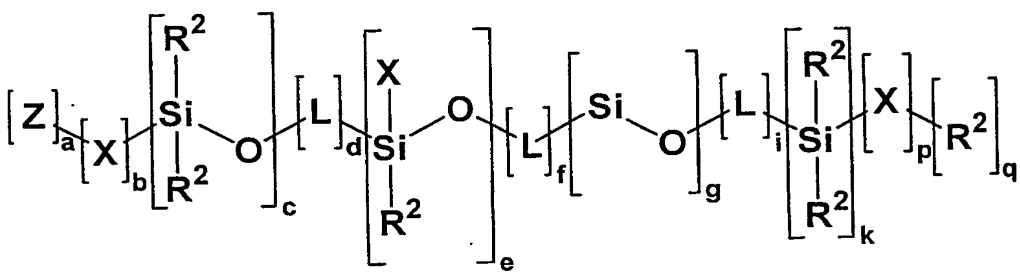
$$B(R^1)_3 \qquad (I)$$

in which each R^1 independently represents an alkyl, aryl, alkylaryl, arylalkyl, cycloalkyl, alkylcycloalkyl or cycloalkylalkyl group which may be unsubstituted or substituted by one or more of the same or different substituents selected from halogen atoms and alkoxy groups;

with an organosilicon compound containing at least one primary, secondary and/or tertiary amino group.

2. A complex as claimed in claim 1, in which each R^1 independently represents a C_{1-10} alkyl group, especially an ethyl, isopropyl, *t*-butyl, *n*-butyl group.

3. A complex as claimed in either claim 1 or claim 2, in which the organosilicon compound has the general formula:

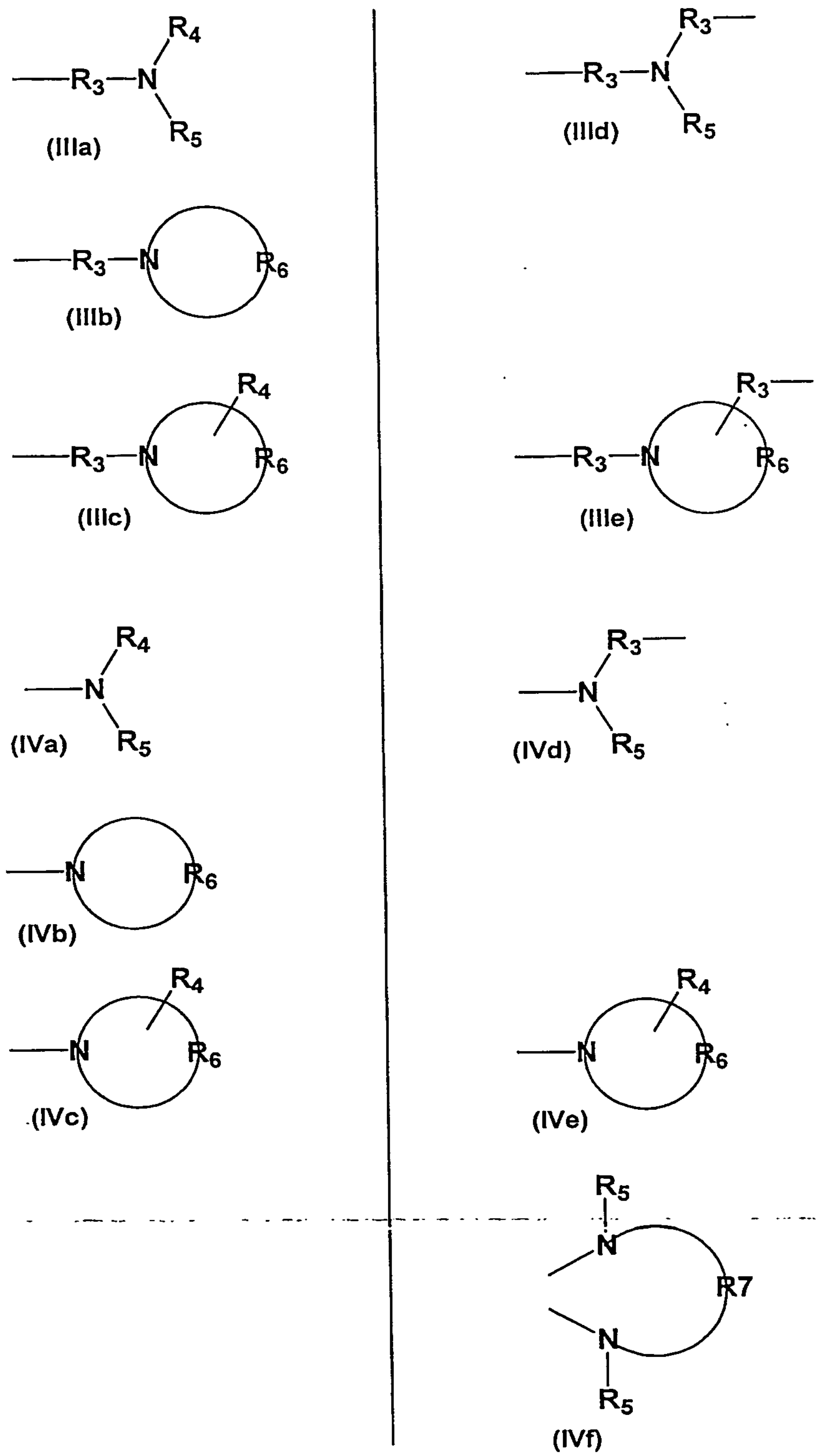


(II)

in which:
a, **q**, are independently equal to 0 or 1;
b, **c**, **d**, **e**, **f**, **g**, **i**, **k**, **p**, are independently equal to or higher than 0;
(**a**, **c**, **e**, **g**, **k**, <u>cannot</u> be all equal to 0 at the same time. <u>At least</u> one of them should be higher than 0 and at least one of the **b**, **d**, **f**, **i**, **p** should be equal to or higher than 1).

each R^2 independently represents a hydrogen atom or a hydroxyl group or an alkyl (e.g. isopropyl, isobutyl, isooctyl, propylisobutyl, etc.), fluoroalkyl, glycidyl alkyl, acrylalkyl, (meth)acrylalkyl, alkoxy, alkoxyalkyl, alkenyl, cycloalkyl (e.g. cyclohexyl, propylcyclohexyl, etc.), aryl, alkyloxyaryl, aryloxyalkyl or alkyloxycycloalkyl-group, each of which may be optionally substituted by one or more primary, secondary or tertiary amino groups and/or other functional groups such as hydroxyls, carbonyls; and
each X (which can be monovalent or divalent depending on the values of a, c, d, e, f, g, i, k, and q) independently represents a group of the general formulae (III) and (IV):

monovalent X | divalent X



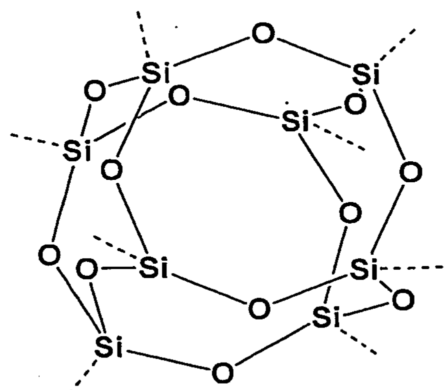
in which R^3 represents an alkylene, alkenyl, phenylene or cycloalkylene group; and each of R^4 and R^5 independently represents a hydrogen atom, a hydroxyl group, or an alkyl, aryl, silylalkyl, silylaryl, cycloalkyl, arylalkyl, alkylaryl, cycloalkylalkyl, alkylcycloalkyl, eterocyclic (saturated or unsaturated), phenyl (Ph-), phenoxy (Ph-O-), or Ph-(C=O)- group each of which may be optionally substituted by one or more primary, secondary or tertiary amino groups and/or other functional groups such as

hydroxyls, carbonyls, etc., R^4 and R^5 can independently be also R^2, R^6 can be a "cyclic" group that means a closed ring hydrocarbon group that is classified as an alicyclic group, aromatic group, or eterocyclic (saturated or unsaturated) group and each one of them can be mono-, di-, tri-, tetra-, penta-substituted by R^3 or R^4 groups (structures IIIc, IIIe, IVc and IVe described only the mono-substituted derivatives). X can also contain organic groups or organic linking groups can include heteroatoms (e.g. O, S, Si atoms) such as in the case of heterocyclic compounds as well as functional groups (e.g. carbonyl, hydroxyl groups, etc).

R^7 can be a "cyclic" of the structure $-Si(R^2)-[Si(R^2)_2-NH-]_n-Si(R^2)-$, where n is equal to or higher than 1.

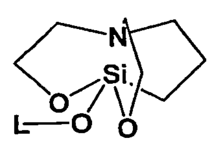
in which L represents:
A monovalent or divalent (depending on the values of the a, b, c, e, g, k, p and q) group and can be independently selected from any of the groups representing the X group or it can also be R^2 or R^3 or R^5 or R^4 or R^6 or R^7 or any polymeric/oligomeric organic mono- or di-radical.

in which Z represents:



where every silicon atom forms a bond (represented by the dashed lines on the above drawing) with either X or R^2 or R^4 or R^5 and at least one silicon atom must be bonded with one X.

4. A complex as claimed in either claim 1 or claim 2, in which the organosilicon compound has the general formula:



(V)

in which L has the meaning given in claim 3.

5. A complex as claimed in claim 3, in which the organosilicon compound has the formula derived from the general formula II for b=1, c=1, q=1 and a, d, e, f, g, i, k, p, q are all independently equal to 0 and where X and R^2 groups are as defined in claim 3.

6. A complex as claimed in claim 3, in which the organosilicon compound has the formula derived from the general formula II for b=1, c>1, e>1, k=1, p=1 and a, d, f, g, i, q are all independently equal to 0 and where X and R^2 groups are as defined in claim 3.

7. A complex as claimed in claim 3, in which the organosilicon compound has the formula derived from the general formula II for a=1, b=1 and c, d, e, f, g, i, k, p, q are all independently equal to 0 and where X group is as defined in claim 3.

8. A complex as claimed in claim 3, in which the organosilicon compound can be a mixture of at least two compounds as any of those claimed in claims 5 to 7.

9. A complex as claimed in claim 3, in which the organosilicon compound is 3-(2-aminoethylamino)propyltrimethoxy silane; 3-(2-aminoethylamino)propyltriethoxy silane; (aminopropyl)trimethoxy silane; (aminopropyl)triethoxy silane; (aminomethyl)trimethoxy silane; (aminomethyl)triethoxy silane; (N-cyclohexylaminomethyl)trimethoxy silane; (N-cyclohexylaminomethyl)triethoxy silane; (N-phenylaminomethyl)trimethoxysilane; (N-phenylaminomethyl)methyldimethoxysilane; (N,N-dimethylaminopropyl)trimethoxysilane; Bis[(3-trimethoxysilyl)propyl]ethylenediamine; N-(3-triethoxysilylpropyl)4,5-dihydroimidazole; 2-(trimethoxysilylethyl)pyridine; Bis(p-aminophenoxy)dimethylsilane; Bis(p-aminophenoxy)dimethylsilane; Bis(dimethylamino)diethylsilane; Ureidopropyltrimethoxysilane; Bis(N-methylbenzamido)ethoxymethylsilane; Octamethylcyclotetrasilazane; 1,3-Bis(3-aminopropyl)tetramethyldisiloxane; an amino functionalised silicone fluid; an amino functionalized silica gel; an amino functionalized-POSS; or an amino/imino functionalized POSS as well as a mixture of at least two of the above.

10. A complex as claimed in claim 4, in which the organosilicon compound is hydroxyethoxysilatrane.

11. The use of a complex as claimed in any one of claims 1 to 10 as an initiator for the polymerisation of a radically polymerisable monomer or oligomer.

12. The use of a complex as claimed in any one of claims 1 to 10 as a primer for activating a surface.

13. The use of a complex as claimed in claim 12, in which the surface has low surface energy and comprises of polyethylene, polypropylene, copolymers of a-olefins, fluorinated polymers (e.g polytetrafluoroethylene, etc.) and other polymers of comparable or higher surface energy.

14. The use of a complex as claimed in claim 12, in which the surface can be selected from the group of homo- or co-polymers of methyl methacrylate, polycarbonate, poly(vinyl chloride), acrylonitrile-butadiene-styrene and other plastics of comparable or higher surface energy.

15. The use of a complex as claimed in claim 12, in which the surface can be selected from the group of thermoplastics, thermosets, wood, composites, ceramics, glass, concrete, and metals.

16. A process for the preparation of a complex as claimed in any of claims 1 to 10, which comprises contacting a solution of an organoborane compound of the general formula (I) with an organosilicon compound containing at least one primary, secondary or tertiary amino group.

17. A process for the preparation of a complex as claimed in any of claims 1 to 10, which comprises contacting a solution of an organoborane compound of the general formula (I) with an organosilicon compound that has the general formula II.

18. A process for the preparation of a complex as claimed in any of claims 1 to 10, which comprises contacting a solution of an organoborane compound of the general formula (I) with an organosilicon compound that has the general formula V.

19. A process for the preparation of a complex as claimed in any of claims 1 to 10, which comprises contacting a solution of an organoborane compound of the general formula (I) with an organosilicon compound as those claimed in any one of the claims 3 to 10.

20. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10 and at least one radically polymerisable monomer and/or oligomer.

21. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10 and at least one radically polymerisable monomer and/or oligomer.

22. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

23. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10, a solvent and at least one radically polymerisable monomer and/or oligomer.

24. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10, a solvent, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

25. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

26. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10, a solvent and at least one radically polymerisable monomer and/or oligomer.

27. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10, a solvent, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

28. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complex upon contact and at least one radically polymerisable monomer and/or oligomer.

29. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complexes upon contact and at least one radically polymerisable monomer and/or oligomer.

30. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complexes upon contact, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

31. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complexes upon contact, a solvent and at least one radically polymerisable monomer and/or oligomer.

32. A polymerisable composition, which comprises a complex as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complexes upon contact, a solvent, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

33. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complexes upon contact, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

34. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complexes upon contact, a solvent and at least one radically polymerisable monomer and/or oligomer.

35. A polymerisable composition, which comprises a mixture of complexes as, claimed in any one of claims 1 to 10, at least one decomplexing agent capable of releasing the organoborane compound from the complexes upon contact, a solvent, a reactive or non-reactive diluent and at least one radically polymerisable monomer and/or oligomer.

36. A polymerizable composition as claimed in any one of the claims 20 to 27, in the form of a one-component composition.

37. A polymerizable composition as claimed in any one of the claims 20 to 35, in the form of a two-component composition in which the first part comprises at least one complex as claimed in any one of the claims 1 to 10 and a second part comprises at least one radically polymerizable monomer and/or oligomer.

38. A polymerizable composition as claimed in any one of the claims 20 to 35, in the form of a two-component composition in which the first part comprises at least one complex as claimed in any one of the claims 1 to 10 and a second part comprises at least one decomplexing agent capable of releasing the organoborane compound from the complex(es) upon contact and at least one radically polymerizable monomer and/or oligomer.

39. A polymerizable composition as claimed in any one of the claims 20 to 35, in which polymerization may be initiated by the supply of energy.

40. A polymerizable composition as claimed in any one of the claims 20 to 35, in which polymerization may be initiated by heating, or by the application of actinic radiation or by electromagnetic radiation or by magnetic radiation, electrical current, ultrasounds, ultraviolet radiation combinations thereof or any other means that result to the aforementioned specie of radiation or heat.

41. A composition as claimed in any one of claims 20 to 35, in which the radically polymerisable monomer and/or oligomer is an olefinically unsaturated system.

42. A composition as claimed in any one of claims 20 to 35, in which the radically polymerisable monomer and/or oligomer is an olefinically unsaturated system selected from the compounds described in detail in the embodiment of the present application (§ Polymerizable Monomers/Oligomers).

43. A composition as claimed in claim 42, in which the radically polymerisable monomer and/or oligomer comprises an acrylate and/or a methacrylate.

44. A composition as claimed in claim 43, in which the radically polymerisable monomer and/or oligomer comprises any compounds selected from the following group: 2-ethylhexyl methacrylate, 2-ethylhexyl methacrylate, 2-ethoxyethyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, isooctyl acrylate, isooctyl methacrylate, isobutyl methacrylate, n-butyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate, n-hexyl methacrylate, isobornyl methacrylate, isodecyl methacrylate and isodecyl acrylate.

45. A composition as claimed in any one of the claims 20 to 44, which also contains at least one of the following: i) pigments, ii) colorants, iii) UV-stabilizers, iv) inhibitors, v) moisture scavengers, vi) free-radical initiators other than organoborane (e.g. organic peroxides, hydroperoxides etc.), vii) sulfonated aromatic polymers, viii) epoxy compounds, ix) epoxy-terminated amine-epoxy adducts, x) additional crosslinking agents, xi) phosphorous containing compounds that contain at least one P-OH group, xii) substances for modifying the curing kinetics ("modifiers") (e.g. metal salts etc.), xiii) rheology control substances (thickeners or thinners) (flow modifiers), xiv) various kinds of silica (e.g. finely divided silica, fumed silica, micro ionized silica, etc.), xv) volatile liquids, xvi) elastomeric materials, xvii) ceramic particles, xviii) glass beads, xix) fluoropolymer powders, xx) microspheres (e.g. glass, thermoplastic resin, ceramic or carbon, solid or hollow, expanded or expandable), xxi) catalysts for epoxy or isocyanate type reactions, xxii) solvents, xxiii) reactive or non reactive diluents (e.g. 1,4-dioxo-2-butene functional materials, aziridine functional materials, various waxes etc.), xxiv) fillers (e.g. alumina, glass powder, ceramic powder, metal powder, etc.), xxv) reinforcement fibres/agents, xxvi) silicone rubbers, xxvii) silicone core-shell particles, xxviii) plasticizers , xxix) adhesion promoters, xxx) antifoaming agents, xxxi) leveling agents, xxxii) modified sand, xxxiii) antioxidants, xxxiv) flame retardants.

46. A composition as claimed in any one of the claims 20 to 45, which also contains other additives commonly used and known in the art of adhesives, sealants, paints, coatings, stain

blocking compositions, casting resins, in shapable moulding materials, in finished mouldings or in composite materials.

47. A composition as claimed in any one of the claims 20 to 46, which also contains one or more additions, preferably a natural nanoclay or a nano-organoclay.

48. A composition as claimed in any one of the claims 20 to 47, which also contains one or more additions, preferably natural montmorillonite or intercalated montmorillonite.

49. A composition as claimed in any one of the claims 20 to 48, which also contains trimethylolpropane tris(2-methyl-1-aziridinepropionate).

50. A composition as claims in any one of the claims 20 to 49, which also contains at least one material that manages the heat of polymerization reaction such that adhesion to the substrates is maintained.

51. A polymeric composition as claimed in any of the claims 20 to 50, in which the concentration of complex is sufficient to provide 0.001 to 10.0%w, preferably 0.002 to 7.0%w, and most preferably 0.003 to 5.0% of boron, based on the total weight of the composition.

52. A method of adhesively bonding at least two substrates together, which comprises applying a polymerisable composition as claimed in any one of claims 20 to 51 to a first substrate, positioning a second substrate in contact with the first substrate via said product, and allowing or causing said composition to cure.

53. A method of adhesively bonding at least two substrates together, which comprises applying a complex as claimed in any one of claims 1 to 10 to the surface of a substrate; subsequently applying a composition comprising a radically polymerisable monomer or oligomer to the thus-primed surface; and subsequently applying a second substrate.

54. A method of adhesively bonding at least two substrates together as claimed in claim 52, in which the second substrate is similarly treated.

55. A method of adhesively bonding at least two substrates together as claimed in claim 53, in which the second substrate is similarly treated.

56. A method of adhesively bonding at least two substrates independently selected from the group of thermoplastics, thermosets, wood, composites, ceramics, glass, concrete, and metals.

57. A method as claimed in any one of the claims 52 to 56, in which at least one substrate is a low surface energy substrate.

58. A method as claimed in claim 57, in which said low surface energy substrate comprises polyethylene, polypropylene, copolymers of a-olefins, or fluorinated polymers (e.g polytetrafluoroethylene, etc.) and other plastics of comparable or higher surface energy.

59. A method as claimed in claim 57, in which said substrates comprises homo- or co-polymers of methyl methacrylate, polycarbonate, poly(vinyl chloride), acrylonitrile-butadiene-styrene and other plastics of comparable or higher surface energy.

60. A method as claimed in any of the claims 52 to 59, wherein any of the two-component polymeric compositions as claimed in any one of the claims 20 to 51 is premixed via preferably a suitable dispenser.

61. A method as claimed in any of the claims 52 to 59, wherein any of the two-component polymeric compositions as claimed in any one of the claims 20 to 51 is applied on the substrates without premixing.

62. The use of compositions as claimed in any one of claims 20 to 51 in the preparation of adhesives, sealants, paints, coatings, stain blocking compositions, casting resins, in shapable moulding materials, in finished mouldings or in composite materials.

63. A polymeric adhesive composition according to any of the claims 20 to 51 wherein the said composition is a two-part curable adhesive composition comprising: a) a first part comprising at least one radically polymerizable monomer/oligomer and at least one decomplexer and b) a second part comprising at least one of any of the complexes as claimed in any one of the claims 1 to 10.

64. A polymeric adhesive composition according to claim 63, wherein the first part and the second part are combined in a whole number ratio of 1:1 to 35:1 and more preferably of 2:1 to 25:1 and most preferably 4:1 to 10:1.

65. A polymeric adhesive composition according to claims 63 and 64 wherein the first part and second part are each in a different receptacle of a two-part adhesive dispenser.

66. An object which incorporates a composition as claimed in any one of claims 20 to 51, whether as a moulding, coating, paint, sealant, ink or adhesive.

S/O

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